

# HomeChemLab.com

## **Illustrated Guide to Home Chemistry Experiments: All Lab, No Lecture**

### **Answer Guide**

Version 1.00  
1 June 2008

This document is updated as necessary to incorporate corrections and suggestions from readers. HomeChemLab.com subscribers automatically receive all such updates by email. If you find an error or have a suggestion for improving this document, please send email to [thompson@homechemlab.com](mailto:thompson@homechemlab.com).

This document is copyrighted, and may not be copied or distributed. If you obtained your copy of this document other than by subscribing to HomeChemLab.com, please visit <http://www.homechemlab.com> and subscribe.

**Copyright © 2008 by Robert Bruce Thompson. All Rights Reserved.**

## **Table of Contents**

### Chapter 6 – Separating Mixtures

- 6.1: Differential Solubility: Separate Sand and Sucrose
- 6.2: Distillation: Purify Ethanol
- 6.3: Recrystallization: Purify Copper Sulfate
- 6.4: Solvent Extraction
- 6.5: Chromatography: Two-Phase Separation of Mixtures
- 6.6: Determine the Formula of a Hydrate

### Chapter 7 – Solubility and Solutions

- 7.1: Make Up a Molar Solution of a Solid Chemical
- 7.2: Make Up a Molal Solution of a Solid Chemical
- 7.3: Make Up a Molar Solution of a Liquid Chemical
- 7.4: Make Up a Mass-to-Volume Percentage Solution
- 7.5: Determine Concentration of a Solution by Visual Colorimetry

### Chapter 8 – Colligative Properties of Solutions

- 8.1: Determine Molar Mass by Boiling Point Elevation
- 8.2: Determine Molar Mass by Freezing Point Depression
- 8.3: Observe the Effects of Osmotic Pressure

### Chapter 9 – Introduction to Chemical Reactions and Stoichiometry

- 9.1: Observe a Composition Reaction
- 9.2: Observe a Decomposition Reaction
- 9.3: Observe a Single-Displacement Reaction
- 9.4: Stoichiometry of a Double Displacement Reaction

### Chapter 10 – Reduction-Oxidation (Redox) Reactions

- 10.1: Reduction of Copper Ore to Copper Metal
- 10.2: Observe the Oxidation States of Manganese

### Chapter 11 – Acid-Base Chemistry

- 11.1: Determine the Effect of Concentration on pH
- 11.2: Determine the pH of Aqueous Salt Solutions
- 11.3: Observe the Characteristics of a Buffer Solution
- 11.4: Standardize a Hydrochloric Acid Solution by Titration

### Chapter 12 – Chemical Kinetics

- 12.1: Determine the Effect of Temperature on Reaction Rate

[12.2: Determine the Effect of Surface Area on Reaction Rate](#)

[12.3: Determine the Effect of Concentration on Reaction Rate](#)

[12.4: Determine the Effect of a Catalyst on Reaction Rate](#)

#### [Chapter 13 – Chemical Equilibrium and Le Chatelier's Principle](#)

[13.1: Observe Le Chatelier's Principle in Action](#)

[13.2: Quantify the Common Ion Effect](#)

[13.3: Determine a Solubility Product Constant](#)

#### [Chapter 14 – Gas Chemistry](#)

[14.1: Observe the Volume-Pressure Relationship of Gases \(Boyle's Law\)](#)

[14.2: Observe the Volume-Temperature Relationship of Gases \(Charles's Law\)](#)

[14.3: Observe the Pressure-Temperature Relationship of Gases \(Gay-Lussac's Law\)](#)

[14.4 Use the Ideal Gas Law to Determine the Percentage of Acetic Acid in Vinegar](#)

[14.5: Determine Molar Mass from Vapor Density](#)

#### [Chapter 15 – Thermochemistry and Calorimetry](#)

[15.1: Determine Heat of Solution](#)

[15.2: Determine the Specific Heat of Ice](#)

[15.3: Determine the Specific Heat of a Metal](#)

[15.4: Determine the Enthalpy Change of a Reaction](#)

#### [Chapter 16 – Electrochemistry](#)

[16.1: Produce Hydrogen and Oxygen by Electrolysis of Water](#)

[16.2: Observe the Electrochemical Oxidation of Iron](#)

[16.3: Measure Electrode Potentials](#)

[16.4: Observe Energy Transformation](#)

[16.5: Build a Voltaic Cell](#)

[16.6: Build a Battery](#)

#### [Chapter 17 – Photochemistry](#)

[17.1: Photochemical Reaction of Iodine and Oxalate](#)

#### [Chapter 18 – Colloids and Suspensions](#)

[18.1: Observe Some Properties of Colloids and Suspensions](#)

[18.2: Produce Firefighting Foam](#)

[18.3: Prepare a Gelled Sol](#)

#### [Chapter 19 – Qualitative Analysis](#)

[19.1: Using Flame Tests to Discriminate Metal Ions](#)

[19.2: Using Borax Bead Tests to Discriminate Metal Ions](#)

[19.3: Qualitative Analysis of Inorganic Anions](#)

[19.4: Qualitative Analysis of Inorganic Cations](#)

[19.5: Qualitative Analysis of Bone](#)

#### [Chapter 20 – Quantitative Analysis](#)

[20.1: Quantitative Analysis of Vitamin C by Acid-Base Titration](#)

[20.2: Quantitative Analysis of Chlorine Bleach by Redox Titration](#)

[20.3: Quantitative Analysis of Seawater](#)

#### [Chapter 21 – Synthesis of Useful Compounds](#)

[21.1: Synthesize Methyl Salicylate from Aspirin](#)

[21.2: Synthesize Rayon Fiber](#)

#### [Chapter 22 – Forensic Chemistry](#)

[22.1: Use the Sherlock Holmes Test to Detect Blood](#)

[22.2: Perform a Presumptive Test for Illicit Drugs](#)

[22.3: Reveal Latent Fingerprints](#)

[22.4: Use the Marsh Test to Detect Arsenic or Antimony](#)

## Chapter 6 – Separating Mixtures

### Laboratory 6.1: Differential Solubility: Separate Sand and Sucrose

Q1: After this procedure, you should end up with separate piles of sand and sucrose with masses that are the same as the initial masses. How closely do your experimental results correspond to the expected results? Propose an explanation for why the final masses of the sand and/or sucrose might be higher or lower than the starting masses.

Answers will vary, but at least 95% of the initial masses of the sand and sucrose should be recovered. There are several likely causes of errors:

- Weighing errors – obviously if errors are made in determining the initial and/or final masses of the sand or sucrose, those final masses may be higher or lower than expected.
- Handling errors – any spillage or other loss of either the sand or the sucrose solution causes corresponding errors in the final masses of the separated compounds.
- Sucrose loss – some sucrose mass may be lost if all of the liquid is not separated from the sand. This source of error can be minimized by rinsing the sand repeatedly with plain water and adding the rinses to the sucrose solution. Also, a small amount of sucrose may be absorbed by the filter paper. Again, repeated rinses minimize this source of error.
- Sucrose gain – if the sand contains soluble impurities, such as sodium chloride (salt), those impurities will be dissolved and added to the mass of the sucrose.
- Sand gain – if the sand is not dried thoroughly before its final mass is determined, the final mass will be higher than expected. Similarly, if not all of the sucrose is extracted from the sand, the mass of that remaining sucrose will be counted as sand mass.

Q2: You are mixing concrete, but the only sand available is heavily contaminated with salt, which weakens concrete. You have plenty of water available, but no means of filtering. How might you remove the salt from the sand?

Sand is insoluble in water, while salt (sodium chloride) is freely soluble. To remove salt, you can simply add water to the sand, agitate the mixture, allow the sand to settle out, and decant or draw off the supernatant liquid, which is an aqueous solution of salt. To remove as much salt as possible, use a large volume of water, rinse the sand repeatedly, and remove as much of the salt solution as possible before doing the next rinse.

Q3: You are presented with a mixture of two compounds, both of which are freely soluble in water. What might you do to separate these compounds using differential solubility?

Use a different solvent, one in which one of the compounds is freely soluble and the other is insoluble.

## Laboratory 6.2: Distillation: Purify Ethanol

Q1: Would you expect the density of the distilled ethanol solution to be lower or higher than the density of the original ethanol solution? Why?

Lower. The distilled alcohol solution contains a higher concentration of ethanol than the original solution. The density of ethanol is lower than the density of water. Therefore, a solution with a higher concentration of ethanol is less dense than a solution with a lower concentration of ethanol.

Q2: Using values for the densities of various concentrations of ethanol and water that you obtain from the CRC handbook or a reliable on-line source, estimate the ethanol concentrations in the original solution and the distillate.

Answers will vary.

Q3: A drugstore offers denatured ethanol in concentrations of 70%, 95%, and 99% by weight. The 70% and 95% solutions are relatively inexpensive, but the 99% solution is very costly. Why?

The 70% and 95% solutions can be produced by distillation or by diluting a more concentrated ethanol solution with pure water. The 99% solution cannot be produced by distillation because ethanol and water form a low-boiling azeotropic mixture at 95.6% ethanol by mass. The only way to remove the additional water necessary to produce 99% ethanol is to use chemical drying agents such as anhydrous calcium chloride or calcium oxide, which is a much more expensive process than distillation.

Q4: Distilling wine produces not colorless pure ethanol as you might expect, but brandy, which is deeply colored and contains complex flavors. Why?

Many of the complex organic compounds that provide the color and flavor of wine are at least as volatile as ethanol, and so cannot be removed by distillation.

## Laboratory 6.3: Recrystallization: Purify Copper Sulfate

Q1: The solubility of copper sulfate pentahydrate is 2033g/L at 100 °C, which means that 305 g should dissolve in 150 mL of water at 100 °C. Why do you suppose we used only 250 g of crude copper sulfate rather than 305 g?

We wanted all of the copper sulfate to remain in solution until we were ready for it to begin crystallizing. If we'd used 305 g of copper sulfate, we would have produced a solution that was saturated at 100 °C. The moment that solution began to cool, copper sulfate would have begun to crystallize out. When we poured the hot solution into the funnel, crystals would form on the funnel and filter paper. Using only 250 g of copper sulfate allowed all of the compound to remain in solution until filtration was complete.

Q2: We obtained about an 80% yield (roughly 200 g of purified copper sulfate from 250 g of crude copper sulfate). We might have improved the percent yield somewhat by dissolving more than 250 g of crude copper sulfate initially, but at best that method

would still result in about a sixth of the crude copper sulfate going to waste. What method might we use to obtain much higher percent yields?

Recycle the waste solution of copper sulfate. When you have purified the first batch of copper sulfate crystals, filter or decant off the supernatant liquid. Heat it to 100 °C, dissolve additional copper sulfate in the hot solution, and allow it to cool, whereupon about 5/6 of the total copper sulfate crystallizes. But because the 1/6 that is retained in the waste solution was already in the solution to start with, essentially all of the copper sulfate you added crystallizes out.

Depending on the initial purity of the copper sulfate, you can repeat this process several times before the concentration of the contaminants in the waste solution becomes too high. If you recycle the waste copper sulfate solution five times, for example, you reduce the total waste from about 1/6, or about 17%, to about 1/30, or about 3.3%. By working carefully, you can increase your overall yield from perhaps 80% to 95% or more.

Q3: A chemist requires copper sulfate of at least 99.9% purity for a particular procedure. She recrystallizes crude copper sulfate as we have done, but analysis shows that her purified copper sulfate is only 99.4% pure. What might she do to obtain copper sulfate of 99.9% or higher purity?

Re-recrystallize the 99.4% copper sulfate. If the first recrystallization reduces the level of impurities by 94%, for example, a second recrystallization may also reduce the level of impurities by 94%, but this time starting from a base that is only 6% as large as the original. Using these percentages, for example, if the original sample contained 10% impurities, the first recrystallization might remove 94% of that 10%, making the recrystallized product 99.4% pure. Recrystallizing the 99.4% pure product might remove 94% of the remaining 0.6% impurities, leaving the final product after two recrystallizations 99.964% pure. (The actual percentage improvement varies according to the chemical you are recrystallizing and many other factors, and will not necessarily be identical for the second and later recrystallizations.)

## Laboratory 6.4: Solvent Extraction

Q1: The colors of the two layers after agitating and settling make it clear that most of the iodine was extracted from the aqueous layer into the organic layer, but that does not explain the color change from orange in the aqueous layer to magenta in the organic layer. Use the Internet to research the cause for this color change.

In aqueous or ethanol solutions, iodine combine with iodide ions to form triiodide ( $I_3^-$ ) ions, which are brown. In many organic solvents, dissolved iodine is present in molecular form, which gives these solutions a violet/magenta color.

Q2: You are running a solvent extraction to isolate the products of a synthesis, using an aqueous layer and an organic layer. After agitation and settling, the two layers are of very similar appearance. You know that the organic layer contains your product and the

aqueous layer is the waste layer, but you are not 100% certain which layer is which. What simple test might you perform to determine which is the organic layer?

Add a drop of water to one of the layers. If the drop of water mixes with the layer, that layer is aqueous. If the water doesn't mix, the layer is organic.

## **Laboratory 6.5: Chromatography: Two-Phase Separation of Mixtures**

Q1: What is the purpose of chromatography?

To separate two or more components of a mixture.

Q2: By what mechanism does chromatography separate the components of a mixture?

Chromatography depends on the fact that different compounds have different affinities for the chosen stationary phase and mobile phase. A component that is relatively more attracted to (more tightly bound to) the stationary phase than to the mobile phase migrates a shorter distance, and vice versa. Polar components of the mixture are more tightly bound to polar solvents such as water and ethanol, and non-polar components are more tightly bound to non-polar solvents such as benzene and alkanes.

Q3: Why did we use a pencil rather than a pen to label and mark the chromatography paper?

A pencil mark is graphite (carbon), which is insoluble, while the dyes used in pens are soluble to a greater or lesser degree in most common chromatography solvents. If we used a pen, the dyes that made up the ink would be separated by the solvent.

Q4: Why should the solvent front be marked immediately after the chromatograph develops?

If you wait until the solvent evaporates, the maximum distance traveled by the solvent front may (will probably be) impossible to determine because the evaporated solvent leaves no mark.

Q5: Define the term  $R_f$  value.

This value is the numeric ratio between the distance traveled by the compound and the maximum distance traveled by the solvent front. The  $R_f$  value is different for different compounds, stationary phases, and mobile phases, and cannot be compared unless all variables are identical.

Q6: How is  $R_f$  value calculated?

Measure the distance from the start line to the center of the mark formed by the component in question. Measure the distance from the start line to the line of the maximum extent of the solvent front. Divide the first value by the second value. For example, if one component migrated 6.3 cm and the maximum extent of the solvent front was 10.0 cm, the  $R_f$  value is calculated as  $6.3 \text{ cm} / 10.0 \text{ cm} = 0.63$ .



Q7: On a particular chromatogram, the solvent front moved 9.5 cm from the point of application and one of the components moved 6.2 cm from the point of applications. What is the  $R_f$  value for that component?

$$6.2 \text{ cm} / 9.5 \text{ cm} = 0.65+$$

Q8: Two of the components of an analyte mixture have  $R_f$  values of 0.25 and 0.83. Which of these components is more soluble in the mobile phase? How do you know?

The component with the  $R_f$  value of 0.83 is more soluble in the mobile phase. One way to look at solubility is as the relative attraction between a solvent and a solute. A solute is more soluble in a solvent for which it has higher attraction (is bound more tightly). The component with an  $R_f$  value of 0.83 is in relative terms more attracted to the solvent than the stationary phase, as compared with the component with an  $R_f$  value of 0.25, which indicates that the former component is more soluble.

Q9: You have run a chromatogram on an analyte mixture in which one of the components remains unidentified. You have calculated an  $R_f$  value for that unknown analyte and are comparing that value against a table of known  $R_f$  values. In addition to the  $R_f$  value itself, what other information do you need about the known value to make your comparison valid? Why do you need this additional information?

You must know what stationary phase and mobile phase was used to determine the known  $R_f$  value.

## Laboratory 6.6: Determine the Formula of a Hydrate

Q1: How does anhydrous copper sulfate differ in appearance from hydrated copper sulfate?

Pure anhydrous copper sulfate is a white powder (a slight blue tint indicates the presence of some hydrated copper sulfate). Hydrated copper sulfate is an intense blue color.

Q2: The formula weight of hydrated copper sulfate is 249.7 grams per mole (g/mol). How many moles of hydrated copper sulfate were present in your sample (Line C of Table 6-7)?

Answers will vary.

Q3: The formula weight of anhydrous copper sulfate is 159.6 g/mol. How many moles of anhydrous copper sulfate were present in your sample (Line E of Table 6-7)?

Answers will vary.

Q4: Would you expect the number of moles of hydrated copper sulfate and the number of moles of anhydrous copper sulfate to be the same? Why or why not?

Yes. Assuming proper technique, none of the copper sulfate is lost, but only water of hydration. If you start with x moles of hydrated copper sulfate, you end with x moles of anhydrous copper sulfate.

Q5: Assuming that all of the mass loss (Line F in Table 6-7) represented water of crystallization, how many moles of water are present in hydrated copper sulfate for each mole of copper sulfate? (Hint: the formula weight of water is 18.015 g/mol. Divide the mass loss by the formula weight of water to calculate the number of moles of water present in the hydrated sample. Divide that number by the number of moles of copper sulfate to determine the proportion of water molecules to copper sulfate molecules and round the result to the nearest whole number.)

The exact numbers will vary, but the rounded value should be five moles of water per mole of copper sulfate.

Q6: How closely did your experimental results correspond to the actual value of five molecules of water per molecule of copper sulfate? Propose several explanations for any variation.

Answers will vary, but if the drying operation is carried out properly and completely, the actual value should be no more than 5% higher than the expected value.

## Chapter 7 – Solubility and Solutions

### Laboratory 7.1: Make Up a Molar Solution of a Solid Chemical

Q1: The molarity of a solution can never be more than a close approximation. List at least five factors that may cause the actual molarity of a solution to differ from the calculated molarity of that solution.

- Mass differences – any mistakes or inaccuracy in weighing the solute changes the actual molarity of the solution.
- Volumetric differences – any mistakes or inaccuracy in measuring the volume of the solution changes the actual molarity.
- Temperature changes – as the temperature of the solution changes, so does the molarity, because the mass of dissolved solute remains constant as the volume of the solution changes with changing temperature.
- Evaporation – if any of the solvent evaporates, the molarity of the solution increases.
- Chemical purity – if your calculations assume 100% purity but you use a chemical that is less than 100% pure, the actual molarity of the solution will be lower than calculated.
- Water of hydration – if you calculate the mass of solute required based on the anhydrous form of a chemical but actually use the hydrated form (or vice versa) the actual molarity of the solution will differ significantly from your calculated value. Note that many chemicals, for example sodium carbonate, exist in two or more hydrated forms with different amounts of water of hydration. These forms may be mixed in one bottle of that chemical, so the only way to make up a solution of that chemical to an accurate molarity is to dry the chemical in an oven or otherwise until it ceases to lose mass. At that point, the chemical is dry, but not necessarily anhydrous. It may instead be in a stable hydrated form, which must be determined before weighing out the solute.
- Absorbed water – some dry chemicals absorb water from the atmosphere. This absorbed water is technically not water of hydration, because it doesn't bind with the chemical in its crystalline structure; it merely leaves the chemical damp. Once again, the only way to make up solutions of accurate molarity of that chemical is to dry it until it ceases to lose mass.

Q2: Although Table 7-1 assumes 100 mL of each solution, there are some solutions, such as silver nitrate, that you may want to make up in smaller batches, because the chemical is expensive or because you expect to use smaller amounts of the solution. Similarly, there are some solutions that you may want to make up in larger batches (e.g., sodium chloride), either because the chemical is inexpensive or because you expect to use larger amounts of the solution. For what other reasons might you decide to make up a smaller or larger batch of a particular solution?

You might make up a smaller batch of a solution because:

- Some solutions have relatively short shelf lives.
- Making up more of a solution than necessary leaves you later with more of the solution to dispose of properly.
- Making up a larger batch of a dilute solution may leave you short of the solid chemical, and you may later need a more concentrated solution of that chemical. It's always much easier to dilute a concentrated solution (or make up the necessary concentration from the solid chemical) than it is to concentrate a dilute solution.
- You may not have sufficient storage space for larger bottles.

You might make up a larger batch of a solution because:

- You need to control the molarity of the solution more closely than is possible with a smaller volume. For example, making up 100 mL of 0.1 M sodium hydroxide requires only 0.399971 g of the salt, whereas making up 1000 mL requires 3.99971 g. If your balance has 0.01 g resolution, the uncertainty for 100 mL of solution is in the second decimal place, versus the third decimal place for 1000 mL of solution. If you make up 1000 mL, you know the actual molarity to one more decimal place than if you make up only 100 mL.

Q3: What characteristic or characteristics of a particular chemical make it easier to obtain a known mass of that chemical by measuring a known volume of a solution of known concentration of that chemical rather than by weighing the solid chemical?

- Some chemicals gain or lose water from the atmosphere. For accurate results with such chemicals, you must dry the chemical thoroughly each time before you weigh a sample. If you make up a solution of known concentration, you can simply use volumetric glassware to measure out a known mass of the chemical to whatever level of accuracy is needed.
- The physical form of some chemicals makes it difficult to weigh a specific amount of the chemical. For example, some chemicals are supplied in the form of pellets, lumps, or large crystals.

## Laboratory 7.2: Make Up a Molal Solution of a Solid Chemical

Q1: In this lab, we made up a 0.5 molal solution of potassium ferricyanide. What additional information would you need to calculate the molarity of that solution? Describe at least two procedures you could use to determine the molarity.

We know the mass of potassium ferricyanide used to make up the solution, so the only additional information we'd need to calculate the molarity is the final volume of the solution. Here are some methods to determine the molarity:

- Measure a known volume of the solution as accurately as possible, for example, using a 10 mL pipette to obtain a 10.00 mL sample of the solution. Evaporate that sample to dryness and determine the mass of potassium ferricyanide it contains. With the volume of sample and mass of the solute in the sample both

known, the molarity can be calculated.

- The total mass of the solution is known (the mass of potassium ferricyanide plus 100.00 g of water.) Measure a known volume of the solution as accurately as possible, for example, using a 10 mL pipette to obtain a 10.00 mL sample of the solution. Determine the mass of that sample. With the total mass of the solution and the mass of a known volume of the solution both known, the total volume of the solution can be calculated. With the total volume of the solution and the total mass of potassium ferricyanide contained in that solution both known, the molarity of the solution can be calculated.
- The total volume of the solution is slightly greater than 100 mL. Transfer the entire solution to a 100 mL volumetric flask, which will be filled to slightly above the index line. Use a pipette carefully to remove just enough of the solution to bring the level down to the index line. Determine how much solution the pipette contains and add that volume to the 100.00 mL contained in the flask (assuming your volumetric flask contains exactly 100.00 mL; see chapter 5 on calibrating your volumetric flask). With the total volume of the solution and the total mass of potassium ferricyanide contained in that solution both known, the molarity of the solution can be calculated.

Q2: After we dissolved the potassium ferricyanide, we did not rinse the beaker to transfer all of the remaining potassium ferricyanide solution quantitatively into the storage bottle. Why?

In making up a solution to a specified molality, we are concerned with the concentration of the solution rather than its volume. Rinsing the beaker and adding the rinse to the storage bottle would increase the volume of the solution, and therefore reduce its molality, by an unknown amount.

Q3: In what circumstances would it be useful to know the molality of a solution rather than its molarity?

Molality is important only when you are working with the colligative properties of solutions.

### **Laboratory 7.3: Make Up a Molar Solution of a Liquid Chemical**

Q1: You need to make up 100 mL of 3 M nitric acid. The concentrated nitric acid you have on hand lists the mass percentage as 68%. Is this sufficient information for you to make up the 3 M bench solution? If not, why? If so, how much concentrated nitric acid would you dilute to make 100 mL of 3 M nitric acid?

Yes, it is sufficient information. The gram molecular mass of nitric acid is 63.013 g/mol, so a 3 M solution contains 189.039 g/L, and 100 mL of that solution contains 18.904 g of nitric acid. Since the mass percentage of the concentrated nitric acid is 68% or 0.68, 1.000 g of that solution contains 0.680 g of nitric acid. Dividing 18.904 g by 0.680 tells us that we need 27.800 g of the concentrated nitric acid to make up 100 mL of 3 M nitric acid.

Q2: You need to make up 100 mL of 0.5 M sulfuric acid. The concentrated sulfuric acid you have on hand lists its density as 1.84 g/mL. Is this sufficient information for you to make up the 0.5 M bench solution? If not, why? If so, how concentrated sulfuric acid would you dilute to make 100 mL of 0.5 M sulfuric acid?

No, it is not sufficient information, because we have no idea what the mass percentage of the concentrated sulfuric acid is. That means we have no idea how much concentrated sulfuric acid to use, either by mass or by volume.

If the bottle label also stated that the mass percentage was 98%, we could determine how much sulfuric acid to use, either by mass (as illustrated in the previous question) or by volume.

- By mass, we know that the gram molecular mass of sulfuric acid is 98.070 g/mol, so a 0.5 M solution contains 49.035 g/L, and 100 mL of that solution contains 4.904 g of sulfuric acid. Since the mass percentage of the acid is 98% or 0.98, 1.000 g of that solution contains 0.980 g of sulfuric acid. Dividing 4.904 by 0.980 tells us that we need 5.004 g of the concentrated sulfuric acid to make up 100 mL of 0.5 M sulfuric acid.
- By volume, we know that the density of the concentrated sulfuric acid is 1.84 g/mL. We need 5.004 g of that solution. Dividing 5.004 g by 1.84 g/mL tells us that we need 2.72 mL of the concentrated acid to make up 100 mL of 0.5M sulfuric acid.

Q3: You have on hand 100 mL of concentrated phosphoric acid. The label lists the mass percentage as 85.0% and the density as 1.68 g/mL. How much 2.00 M phosphoric acid solution could you make up from this amount of the concentrated acid?

At 1.68 g/mL, the 100 mL of concentrated phosphoric acid has a mass of 168 g. With a mass percentage of 85% or 0.85, that 168 g of solution contains  $(168 \text{ g} \times 0.85) = 142.8 \text{ g}$  of phosphoric acid. The gram molecular mass of phosphoric acid is 98.00 g/mol. Dividing the available 142.8 g of phosphoric acid by the gram molecular mass of 98.00 tells us that our sample contains about 1.457 moles of phosphoric acid. Dividing 1.457 moles by the desired molarity of 2.00 mol/L tells us that we have sufficient phosphoric acid to make up about 0.729 L of 2.00 M phosphoric acid.

Q4: You have on hand some concentrated muriatic acid from the hardware store that lists its contents as 31.45% HCl. You want to make up 1 L of 1.00 M HCl, but you are concerned that the mass percentage listed on the bottle may be inaccurate. You tare a 100 mL volumetric flask and use it to determine that 100 mL of your acid has a mass of 116.03 g. Based on that information, is the mass percentage listed on the bottle accurate? If not, by how much does it differ from the actual value?

This is a trick question. If the density and mass percentage are both correct, we can make up a solution of a specified molarity by either mass or volume. However, if the only known value is the density of the solution, we have no way to determine the actual mass percentage or molarity of the concentrated muriatic

acid. That is, of the 116.03 g total mass of our 100 mL sample, we have no way to know how much of that mass is HCl and how much is water.

We can, however, determine the actual concentration of the acid by looking up the density of various concentrations of hydrochloric acid in a reference book. Doing so, we learn that the density of 31% HCl is 1.1540 g/mL and that of 32% HCl is 1.1590 g/mL. Our sample has a density of 1.1603 g/mL, so it clearly has a concentration greater than 32%, rather than the stated value of 31.45%. Looking at the table of densities, we find that 33% HCl has a density of 1.1640 g/mL, so the actual concentration of our acid (density 1.1603 g/mL) must be between 32% and 33%.

By interpolation, we estimate the actual concentration as 32.26%, a 0.81% higher concentration than specified on the label.

### **Laboratory 7.4: Make Up a Mass-to-Volume Percentage Solution**

Q1: What is the molarity of the 1% m/v solution of phenolphthalein solution? Why do you suppose molarity is never used to specify the concentrations of solutions of phenolphthalein and similar indicators?

A 1% m/v solution contains 10 g of phenolphthalein per liter of solution. The gram molecular mass of phenolphthalein is 318.323 g/mol, so one liter of this solution contains  $[10 \text{ g} / 318.323 \text{ g/mol}] = 0.0314+$  moles, which means the molarity of the solution is 0.0314+ M.

Molarity is never used to indicate the concentration of indicator solutions because the indicator is not considered to be one of the reactants. (Although, of course, the indicator does react with ions or molecules in the solution being tested, it is present in such a trivially small amount that it has no practical effect on the stoichiometry of the reaction.)

Q2: For which types of solutions is mass-to-volume percentage a more useful method of specifying concentration than molarity or other methods?

A m/v solution is used for indicators (when the exact number of moles of the substance being added doesn't matter) and in situations where you want to use volumetric methods to measure a specific mass (rather than number of moles) of the solute, such as measuring a specific mass dosage of a liquid medicine by volume.

### **Laboratory 7.5: Determine Concentration of a Solution by Visual Colorimetry**

Q1: We used copper sulfate in this lab because it is strongly colored, inexpensive, and readily available. But colorimetry is not the best method for determining the concentration of a solution of copper sulfate. (We could instead simply evaporate the solution in test tube #6 and determine accurately the mass of the copper sulfate it contains.) Under what circumstances, then, would colorimetry be a good choice for determining the concentration of a solution?

Colorimetry is a good choice when speed and convenience are important. (Evaporating the solution requires more time and effort.) If the solution contains multiple species, only one of which is colored, the concentration of that species can be determined directly, whereas gravimetric methods would require separating the species before determining their concentration gravimetrically. If a solution contains multiple colored species, their concentrations can be determined colorimetrically by determining the percentage absorption at characteristic wavelengths. Finally, colorimetry can be used to determine the concentrations of volatile substances in solution (such as the complex organic species present in wine) that cannot be determined accurately by gravimetric methods.

Q2: List at least five possible sources of error that may occur with this visual colorimetry procedure.

- Mass differences – any mistakes or inaccuracy in weighing the solute used to make up the reference solutions changes the color density.
- Volumetric differences – any mistakes or inaccuracy in measuring the volume of the reference solutions changes the color density.
- Assessment errors – although the human eye is very good at determining small color differences, when two solutions are very close in color density, either may be judged denser than the other.
- Uneven lighting – even small differences in the intensity of the illumination used to observe two samples may lead to incorrect assessments. For example, if you are using a sheet of white paper as a reflective background, if the light source is closer to one side of the paper, tubes assessed on that side will appear to have higher transmission than those more distant from the light source.
- Unequal transmission – one test tube may transmit slightly more light than another.
- Different solution levels – if you compare two identical test tubes, one of which is half full of a solution at a given concentration and the other of which is only one quarter full of the same solution, those tubes may appear to have slightly different levels of transmission. (Try it.)

Q3: You are presented with an unknown solution that contains different concentrations of four food coloring dyes. Could you use visual colorimetry to determine the concentrations of those dyes? Why or why not?

In practical terms, no, it's not possible to use visual colorimetry to determine the concentration of mixed dyes in a solution, because your eyes see the mixed dye solution as having one overall color and density that would be essentially impossible to duplicate by arbitrarily mixing different amounts of different dyes.

If you have an actual colorimeter, it is possible to determine the concentrations of the mixed dyes, because each dye has a characteristic absorption spectrum that can be measured separately by the colorimeter even though the other dyes in the solution interfere with visual colorimetry.



## Chapter 8 – Colligative Properties of Solutions

### Laboratory 8.1: Determine Molar Mass by Boiling Point Elevation

Q1: Name and define the unit of concentration used in calculating values for colligative properties of solutions. Why is this unit of concentration used rather than molarity?

Molality (abbreviated m or mol/kg) is the unit of concentration used for colligative properties calculations. Molality is used because it specifies an exact ratio, independent of temperature, between the number of particles of solute and the number of particles of solvent. Molality is also a more accurate and precise method of specifying concentration, because molality uses purely gravimetric (mass) values, while molarity requires volumetric values. Because balances are available with considerably higher accuracy and precision than volumetric glassware offers, using only a balance to make up solutions by molality allows higher accuracy, which improves the accuracy of colligative properties calculations.

Q2: The  $K_{bp}$  for  $H_2O$  is  $0.512^{\circ}C/molal$ . Applying this value and the van't Hoff factors for sodium chloride (2) and sucrose (1) to the boiling point elevation values you recorded in Table 8-1, calculate the formula weights of sodium chloride and sucrose. Record these calculated values in Table 8.1.

Answers will vary. The actual gram molecular masses are 58.443 g/mol for sodium chloride and 342.29648 g/mol for sucrose.

Q3: What effect on boiling point would you expect if you dissolved sufficient ethanol in water to produce a 1 molal solution?

The boiling point of the ethanol-water mixture is lower than the boiling point of pure water. Boiling point elevation occurs only when the solute is not volatile. Because ethanol is also a volatile solvent, adding ethanol to water does not increase the boiling point.

### Laboratory 8.2: Determine Molar Mass by Freezing Point Depression

Q1: Did all of the solutions you tested freeze? If not, propose and quantify an explanation for this observation.

Answers may vary, depending on the temperature of the ice/salt bath.

The 6 molal solution of sodium chloride has the lowest freezing point, which can be calculated by multiplying the molality (6) by the van't Hoff factor (2) by the freezing point constant for water ( $1.858^{\circ}C/molal$ ) to give an expected freezing point of  $-(6 * 2 * 1.858) = -22.296^{\circ}C$ .

The 3 molal solution of sodium chloride (van't Hoff factor 2) and the 6 molal solution of sucrose (van't Hoff factor 1) have identical freezing points (in theory; experimental results may vary slightly):

$$\text{NaCl} = -(3 * 2 * 1.858) = -11.148\text{ }^{\circ}\text{C}$$

$$\text{Sucrose} = -(6 * 1 * 1.858) = -11.148\text{ }^{\circ}\text{C}$$

as do the 1.5 molal solution of NaCl and 3 molal solution of sucrose:

$$\text{NaCl} = -(1.5 * 2 * 1.858) = -5.574\text{ }^{\circ}\text{C}$$

$$\text{Sucrose} = -(3 * 1 * 1.858) = -5.574\text{ }^{\circ}\text{C}$$

The 1.5 molal solution of sucrose has the highest freezing point:

$$\text{Sucrose} = -(1.5 * 1 * 1.858) = -2.787\text{ }^{\circ}\text{C}$$

Q2: In the early days of automobiles, methanol was used universally as an antifreeze. In 1937, antifreeze solutions based on ethylene glycol were introduced, and quickly gained almost 100% market share, despite the fact that they cost much more than methanol. Propose an explanation for this rapid adoption of ethylene glycol antifreeze solutions. (Hint: look up the physical properties of methanol and ethylene glycol.)

Like methanol, ethylene glycol is miscible with water, so solutions of any molality can be made simply by varying the proportions of water and coolant. The main reason that methanol was quickly abandoned in favor of ethylene glycol is that although methanol is an excellent antifreeze, the very low boiling point of pure methanol (64.7 °C) and methanol/water mixtures makes it a very poor coolant. (Think about all those scenes in old movies that show a radiator boiling over...)

Conversely, ethylene glycol has a high boiling point (197.3 °C, versus 100 °C for pure water), as do mixtures of water and ethylene glycol, so using ethylene glycol prevents both radiator freeze-ups and boil-overs.

Q3: The  $K_{fp}$  for  $\text{H}_2\text{O}$  is 1.858 °C/molal. Applying this value and the van't Hoff factors for sodium chloride (2) and sucrose (1) to the freezing point depression values you recorded in Table 8-1, calculate the formula weights of sodium chloride and sucrose. Record these calculated values in Table 8.1.

Answers will vary. The actual gram molecular masses are 58.443 g/mol for sodium chloride and 342.29648 g/mol for sucrose.

Q4: What effect on freezing point would you expect if you dissolved sufficient ethanol in water to produce a 1 molal solution?

Ethanol does not dissociate in aqueous solution, so its van't Hoff factor is one. The  $K_{fp}$  for water is 1.858 °C/molal, so you would expect a 1 molal solution of ethanol in water to have a freezing point of -1.858 °C.

### Laboratory 8.3: Observe the Effects of Osmotic Pressure

Q1: Calculate the mass gain (or loss) for each of the samples, in grams and percentage, and enter the results in Table 8-3. Note which samples gained mass and which samples lost mass. Propose an explanation.

Exact answers will vary, but samples A through F should lose mass and sample G should gain mass.

Samples A through F are placed in solutions of varying concentration of sodium chloride or sucrose. In this hypertonic environment—one in which the outside solution is more concentrated—water flows outward from the cell, shrinking it and reducing its mass.

Sample G is placed in pure water. In this hypotonic environment—one in which the solution inside the cell is more concentrated—water flows into the cell, swelling it and increasing its mass.

Q2: If you submerged a celery sample in a 70% ethanol solution, would you expect that sample to gain or lose mass? Why?

If you could maintain the sample at constant volume, you would expect its mass to decrease, because osmotic pressure would force ethanol into the cells. Ethanol is less dense than water, so the mass of the sample would decrease.

In practice, you would expect the mass of the sample to increase because the sample swells as it absorbs ethanol and the additional volume counters the lower density of the ethanol.

In reality, it's a close thing. Try it yourself and see how much mass difference you determine experimentally.

Q3: Using only the materials and equipment listed in this chapter, propose an experimental method to accurately determine the concentration of the solution in the celery cells.

Here is one possible procedure:

- Determine and record the mass of a dry sample of celery. That mass includes the solid mass as well as an unknown amount of liquid of unknown molality.
- Submerge the sample in a concentrated solution of known molality (such as the 6 molal solution of sodium chloride). Osmotic pressure forces the molality of the solution inside the celery cells towards the molality of the external solution. (The molality of that solution can be taken as constant, because the amount of water removed from the small sample is trivial compared to the volume of external solution.)
- After the sample has come to equilibrium, remove it from the external solution, rinse it with a small amount of water, and pat it dry with a paper towel.
- Again determine and record the mass of the sample. Any mass loss must be due to water loss from the sample, and the solution inside the celery cells can now be assumed to be 6 molal.
- Dry the sample thoroughly (use an oven if one is available) and again determine and record the mass of the “anhydrous” celery. Any mass loss can be assumed to be water.
- With these three masses known, it is a matter of simple calculation to determine the amount of water present in the sample at each stage, and from that the molality of the solution in the original sample.

## Chapter 9 – Introduction to Chemical Reactions and Stoichiometry

### Laboratory 9.1: Observe a Composition Reaction

Q1: List at least five sources of error in this experiment.

- Weighing errors – any errors in determining the mass of the reactants or products will obviously affect the calculated yield.
- Impurities in the reactants – gross impurities in the reactants (for example, heavy rust on the iron) may result in the iron sulfide having significant impurities.
- Reactants too coarse or not mixed thoroughly – the ideal reaction mixture is very finely divided iron and sulfur, thoroughly mixed before the reaction starts. If one or both of those conditions is not true, some of the iron and/or sulfur may not come into contact with the other reactant and may survive the reaction unchanged.
- Stoichiometric imbalance – if one of the reactants is present in gross excess, it will remain in excess in the product.
- Sulfur loss – sulfur burns in air to form sulfur dioxide, which has a characteristic biting odor. If enough sulfur forms sulfur dioxide, insufficient sulfur may remain to react with all of the iron present, leaving a mix of iron sulfide and metallic iron.
- Product loss – in any vigorous reaction in an open vessel, there is always the risk of losing some of the product from the reaction vessel.

Q2: If you repeated this experiment using 2.0 g of iron and 1.5 g of sulfur as the reactants, would you expect the product to be attracted to a magnet? Why?

No. The atomic mass of iron is 55.847, so 2.0 g of iron is 0.0358+ moles. The atomic mass of sulfur is 32.06, so 1.5 g of sulfur is 0.0467+ moles. Sulfur is present in slight excess, so all of the iron should react to form iron sulfide.

If you used, for example, 3.0 g of iron and only 1.5 g of sulfur, the iron would be present in stoichiometric excess, and the final product would contain a mix of iron sulfide and metallic iron. That product would be attracted to a magnet.

Q3: Upon running this experiment, a student obtains an actual yield of 113.4%. Ruling out weighing errors, what is the most likely source of this error?

The product contains unreacted sulfur and/or iron. For example, if iron is the limiting reagent, the theoretical yield is calculated based on a 1:1 mole ratio of sulfur. If the product contains the expected yield of iron sulfide with unreacted sulfur remaining, the actual yield will be higher than the theoretical yield.

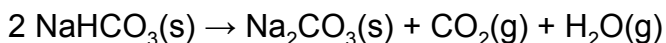
Q4: How might you adjust the conditions of this experiment to maximize the amount of FeS produced as product while minimizing the production of Pyrrhotite ( $\text{Fe}_{(1-x)}\text{S}$ ) and Mackinawite ( $\text{Fe}_{(1+x)}\text{S}$ )?

Use a reaction mixture with as close as possible to a 1:1 mole ratio between iron and sulfur. Also, ideally, we'd like the reactants to be finely ground and intimately mixed, and to run the reaction in a sealed vessel under an inert atmosphere to prevent sulfur from reacting with atmospheric oxygen to form sulfur dioxide.

### Laboratory 9.2: Observe a Decomposition Reaction

Q1: Based on the original mass of sodium hydrogen carbonate used in Part II and the balanced equation, calculate the theoretical yield of sodium carbonate.

Answers will vary depending on the actual mass of sodium hydrogen carbonate used, but based on the balanced equation



two moles of sodium hydrogen carbonate react to form one mole of sodium carbonate.

Accordingly, if the mass of the sodium hydrogen carbonate was 5.00 g, we can calculate as follows:

$$[5.00 \text{ g} / 84.007 \text{ g/mol}] = 0.595+ \text{ moles of sodium hydrogen carbonate}$$

Since the mole ratio of reactant to product is 2:1, our theoretical yield is:

$$[0.595+ \text{ mol} / 2] = 0.297+ \text{ moles of sodium carbonate}$$

Multiplying the expected yield in moles by the gram molecular mass of sodium carbonate gives an expected yield in grams of:

$$[0.297+ \text{ mol} * 105.989 \text{ g/mol}] = 3.15+ \text{ g of sodium carbonate}$$

Q2: Assuming that the product in Part II is pure anhydrous sodium carbonate, calculate the percent yield. Would you expect the actual yield of sodium carbonate to closely approach the theoretical yield? Why or why not?

The actual yield should be quite close to the theoretical yield for this reaction because the decomposition products include only solid sodium carbonate and carbon dioxide and water—both of which are outgassed during heating—so the percent yield should be near 100%. In fact, the apparent percent yield may be higher than 100% if the final product is some mix of anhydrous and hydrated sodium carbonate rather than pure anhydrous sodium carbonate. If that occurs, continue drying the sodium carbonate in the oven until the sample stops losing mass.

### Laboratory 9.3: Observe a Single-Displacement Reaction

Q1: Would you expect the reaction rate of iron with hydrochloric acid to be faster or slower than the rate you observed for aluminum with hydrochloric acid? Why?

Slower, because iron is lower in the reactivity series than aluminum.

Q2: U.S. one-cent coins made after 1982 consist of a zinc core with a thin copper plating. What reaction would you expect if you dropped an uncirculated U.S. cent into

concentrated hydrochloric acid? Why? If testing a badly worn and scratched coin had different results, how would you explain that difference?

You would expect no reaction between the uncirculated one-cent coin and the hydrochloric acid, because copper is an extremely unreactive metal and lies below hydrogen in the reactivity series. You would expect the worn or scratched coin to react with the hydrochloric acid, because the acid would come into contact with exposed zinc, which is a very reactive metal and lies far above hydrogen in the reactivity series.

In fact, if you intentionally scratch a penny to expose the underlying zinc and submerge that scratched coin in concentrated hydrochloric acid, the zinc and acid react with fair vigor to form zinc chloride and hydrogen gas. After some time, all of the zinc reacts, leaving only the thin copper shell of the coin.

Q3: In Part II, if you had submerged a silver teaspoon in a copper sulfate solution, what reaction would you expect? Why?

You would expect no reaction, because copper lies above silver in the reactivity series.

Q4: Brass is an alloy (mixture) of copper metal and zinc metal. If you added brass filings to a solution of concentrated hydrochloric acid, what reaction(s) would you expect to occur and what products would you expect the reaction(s) to produce?

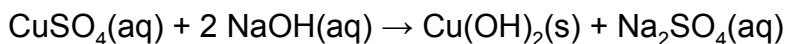
Because copper lies well below hydrogen in the reactivity series and zinc lies well above hydrogen, you would expect the zinc to react with the hydrochloric acid to form zinc chloride and hydrogen gas, and the copper to remain unaffected by the acid.

The acid removes the metallic zinc from the brass filings, leaving only spongy copper behind. Interestingly, this is one method used to produce spongy metal catalysts for such purposes as catalytic converters. The inactive metal, which will be the catalyst, is alloyed with an active metal and then finely divided as a powder or filings. When that finely-divided alloy is reacted with a strong acid, the acid removes the active metal leaving the unreactive metal in spongy form, which increases its surface area dramatically.

## Laboratory 9.4: Stoichiometry of a Double Displacement Reaction

Q1: What are the theoretical mole ratios of copper(II) hydroxide and sodium sulfate?

From the balanced equation for this reaction:

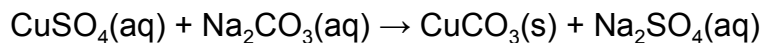


we see that copper(II) hydroxide and sodium sulfate are produced in equimolar amounts, so the mole ratio is 1:1.

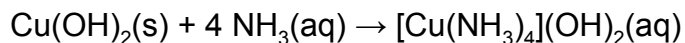
Q2: If you react one mole of sodium hydroxide with excess copper(II) sulfate how many moles of copper(II) hydroxide are produced?

From the balanced equation, we know that two moles of sodium hydroxide are required to produce one mole of copper(II) hydroxide, so one mole of sodium hydroxide produces one half mole of copper(II) hydroxide.

Q3: Write a balanced equation for the reaction of copper(II) sulfate with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) to produce copper(II) carbonate ( $\text{CuCO}_3$ ) and sodium sulfate.



Q4: Write a balanced equation for the reaction of copper(II) hydroxide with aqueous ammonia ( $\text{NH}_3$ ) to produce tetraaminocopper hydroxide.



## Chapter 10 – Reduction-Oxidation (Redox) Reactions

### Laboratory 10.1: Reduction of Copper Ore to Copper Metal

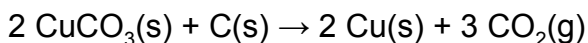
Q1: Observe and describe the appearance of the products after heating the crucible. (If necessary, use a mortar and pestle to crush the product.) Which products can you identify visually?

The exact appearance of the product depends on many factors, including how finely the reactants were divided and mixed, the temperature and duration of heating, how much air was available during the reaction, and so on. Ideally, the product will be a shiny reddish pool of pure molten copper, but your product will probably be a mass of copper metal combined with unreacted charcoal and perhaps a bit of unreacted copper carbonate.

We ran this experiment twice. For the first run, we used the mix shown in the image in the book, with the charcoal and copper carbonate not very finely ground or well mixed. That reaction mixture yielded a pool of metallic copper in the bottom of the crucible with a relatively solid mass of unreacted charcoal on top. For the second run, we used a mortar and pestle to grind the reaction mixture to a fine powder and mixed it thoroughly. That reaction mixture yielded about the same amount of metallic copper on the bottom of the crucible with a crumbly mass of unreacted charcoal on top.

Q2: From the balanced equation for this reaction and knowing that the molar masses of carbon and copper(II) carbonate are 12.01 g/mol and 123.56 g/mol respectively, which reactant was in excess, and by how much? Why might we have chosen to use this reactant in excess?

The exact answer will vary depending on the masses of copper(II) carbonate and charcoal actually used. The balanced equation for the reaction is:



so the mole ratio of copper(II) carbonate to charcoal (carbon) is 2:1.

Assuming 5.00 g of copper(II) carbonate and 3.00 g of carbon, the calculation is as follows:

$$(5.00 \text{ g} / 123.56 \text{ g/mol}) = 0.0405\text{- moles of copper(II) carbonate}$$

Since the mole ratio of copper(II) carbonate to carbon is 2:1, we need only half as many moles of carbon, or:

$$[0.0405\text{- mol} / 2] = 0.0202\text{+ moles of carbon}$$

$$[0.0202\text{+ mol} * 12.01 \text{ g/mol}] = 0.243 \text{ g of carbon}$$

So, at 3.00 g, carbon was in large excess.

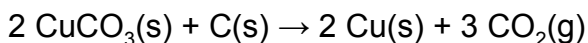
We used carbon in large excess for two reasons. First, we wanted to make absolutely sure that every two molecules of copper(II) carbonate had a carbon



atom with which to react to make sure that all of our copper ore was reduced to metallic copper. Second, at the high temperature inside the crucible, carbon can react directly with atmospheric oxygen to form carbon dioxide, and we expected considerable loss of carbon from that reaction.

Q3: Assuming that the carbon reacted stoichiometrically with the copper(II) carbonate and that none of the carbon reacted with atmospheric oxygen to form carbon dioxide, calculate the expected mass loss. How does the calculated mass loss compare with the mass loss you observed?

The actual mass loss will vary. The theoretical mass loss can be calculated from the balanced equation:



For every two moles of copper(II) carbonate that react, three moles of carbon dioxide gas are lost, or, stated another way, for every mole of copper(II) carbonate that reacts, 1.5 moles of carbon dioxide gas are lost.

The gram molecular mass of carbon dioxide is 44.01 g/mol. Again assuming a 5.00 g sample of copper(II) carbonate, the mass loss can be calculated as follows:

$(5.00 \text{ g} / 125.56 \text{ g/mol}) = 0.0405\text{- moles of copper(II) carbonate}$

$(0.0405\text{- mol} * 1.5) = 0.0607\text{- moles of carbon dioxide}$

$(0.0607\text{- mol} * 44.01 \text{ g/mol}) = 2.67\text{+ grams of carbon dioxide}$

Q4: More than 2,000 years passed from when copper ore was first smelted in about 3500 BC until iron ore was first smelted in about 1200 BC, and another 3,000 years passed before aluminum metal was successfully reduced from aluminum ore in the 19th century? Why did it take so long?

Look at the reactivity series of metals. Aluminum is extremely reactive, iron somewhat reactive, and copper relatively unreactive. In effect, this means that aluminum is very tightly bound in its compounds, iron less so, and copper very loosely.

The practical effect of this is that copper compounds can be reduced to metallic copper at the relatively low heat of wood burning in the open, because the bonds that copper forms in its compounds are weak enough to be broken at the temperature achieved with such a fire. If you placed iron ore and charcoal in a wood fire, you'd find that no reduction occurred because the relatively low temperature of the wood fire is insufficient to break the bonds of iron in its compounds.

To reduce iron ore to metallic iron, we'd need much more extreme conditions, such as a charcoal fire with a bellows supplying additional air to increase the temperature of the fire. It took about two and a half millennia after copper was first accidentally smelted before such equipment became available and the first successful attempt was made to smelt iron.

Aluminum is much more reactive than iron and much more tightly bound in its compounds, enough so that it is effectively impossible to smelt aluminum using only heat. The first practical process for reducing metallic aluminum from ores, and the one still used today, dissolved the aluminum oxide ore in a molten bath of the mineral cryolite, and used electric current to reduce aluminum ions to metallic aluminum metal at an electrode.

### Laboratory 10.2: Observe the Oxidation States of Manganese

Q1: What are the final oxidation states of manganese in test tubes A, B, C, and D?

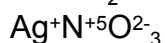
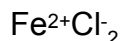
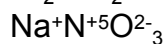
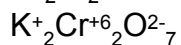
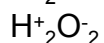
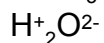
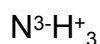
Test tube A: +7

Test tube B: +6

Test tube C: +4

Test tube D: +2

Q2: What are the oxidation states of each atom in the following species:  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{NaNO}_3$ ,  $\text{FeCl}_2$ , and  $\text{AgNO}_3$ ?



## Chapter 11 – Acid-Base Chemistry

### Laboratory 11.1: Determine the Effect of Concentration on pH

Q1: Chart pH against concentration for all five compounds on one piece of graph paper. What do you conclude about the effect of concentration for a strong acid (hydrochloric acid or sulfuric acid) versus a weak acid (acetic acid) and for a strong base (sodium hydroxide) versus a weak base (sodium carbonate)?

Strong acids and strong bases are essentially completely dissociated in all but the most concentrated solutions, which means that the hydrogen ion or hydroxide ion concentration is effectively the same as the concentration of the strong acid or strong base.

Weak acids and weak bases are only partially dissociated in aqueous solutions, which means that the concentration of the hydrogen ions or hydroxide ions is lower than the concentration of the weak acid or base. Accordingly, the pH of an aqueous solution of a weak acid is higher than the concentration of the acid, and the pH of an aqueous solution of a weak base is lower than the concentration of the base. The weaker the acid or base, the greater the difference between the actual pH and the concentration of the acid or base.

Although as an ionic salt sodium carbonate dissociates completely in aqueous solution, it does not contain hydroxide ions. Sodium carbonate functions as a weak base because it dissociates into sodium ions and carbonate ( $\text{CO}_3^{2-}$ ) ions. The carbonate ion is the conjugate base of the weak acid carbonic acid ( $\text{H}_2\text{CO}_3$ ).

Q2: What pH values would you expect for 10 M solutions of hydrochloric acid and acetic acid? Why?

Hydrochloric acid is a strong acid, which means it dissociates completely into hydrogen ions and chloride ions. To calculate pH, we can assume that the hydrogen ion concentration is the same as the concentration of the hydrochloric acid. Accordingly, we can calculate the pH of a 10 M hydrochloric acid solution as follows:

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}[10] = -1$$

Acetic acid is a weak acid, which means that it does not fully dissociate into hydrogen ions and acetate ions. The acid dissociation constant for acetic acid is  $1.74 \cdot 10^{-5}$ . Ignoring the contribution to  $[\text{H}_3\text{O}^+]$  made by water, we can calculate the pH of a 10.0 M solution of acetic acid as follows:

$$K_a = 1.74 \cdot 10^{-5} = ([\text{H}_3\text{O}^+] \cdot [\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}])$$

An unknown amount of the acetic acid has dissociated, which we'll call  $x$ . That means that the concentration of the acetic acid, or  $[\text{CH}_3\text{COOH}]$  is  $(10.0 - x)$ , while the concentrations of the dissociated ions,  $[\text{H}_3\text{O}^+]$  and  $[\text{CH}_3\text{COO}^-]$ , are both  $x$ . Filling in the formula gives us:

$$1.74 \cdot 10^{-5} = ([x] \cdot [x]) / [10.0 - x]$$

or

$$1.74 \cdot 10^{-5} = x^2 / (10.0 - x)$$

or

$$(1.74 \cdot 10^{-5}) \cdot (10.0 - x) = x^2$$

or

$$1.74 \cdot 10^{-5} - (1.74 \cdot 10^{-4} \cdot x) = x^2$$

Solving for x gives us a value of  $4.08524 \cdot 10^{-3}$  or 0.00408524. Knowing that value tells us that the concentration of the hydrogen ion in a 10 M acetic acid solution is 0.00408524 M. We can then calculate the approximate pH of the 10 M acetic acid solution as:

$$\text{pH} = -\log_{10}(0.00408524) = 2.389$$

Q3: If acids A and B have  $\text{pK}_a$  values of -9.32 and 2.74, respectively, which is the stronger acid? Why?

Acid A is an extremely strong acid, while acid B is a relatively weak acid. A value for  $\text{pK}_a$  less than -2 indicates that the acid dissociates almost completely, while a value for  $\text{pK}_a$  greater than -2 indicates that the acid dissociates only partially.

Acids with  $\text{pK}_a$  values higher than -2 are therefore considered weak acids, and those with  $\text{pK}_a$  values less than -2 are considered strong acids.

Q4: The  $[\text{H}_3\text{O}^+]$  of a solution is known to be 0.000413 mol/L. What is the pH of the solution?

$$\text{pH} = -\log_{10}(0.000413) = 3.384$$

Q5: The  $[\text{OH}^-]$  of a solution is known to be 0.000413 mol/L. What is the pH of the solution?

$$[\text{H}_3\text{O}^+] \cdot [\text{OH}^-] = 1 \cdot 10^{-14}$$

$$[\text{H}_3\text{O}^+] \cdot 0.000413 = 1 \cdot 10^{-14}$$

$$[\text{H}_3\text{O}^+] = (1 \cdot 10^{-14}) / 0.000413 = 2.42 \cdot 10^{-11}$$

$$\text{pH} = -\log_{10}(2.42 \cdot 10^{-11}) = 10.616$$

Or, more simply (see the preceding question):

$$14.000 - 3.384 = 10.616$$

Q6: A 0.1 M solution of an acid is found to have a pH of 2.37. What is the  $\text{pK}_a$  of that acid?

The acid, which we can designate HA, dissociates into  $\text{H}^+$  ions and  $\text{A}^-$  ions. With the pH known to be 2.37, we can calculate the concentration of hydrogen ions as follows:

$$\text{pH} = 2.37 = -\log_{10}[\text{H}^+]$$

$$[\text{H}^+] = 0.00427$$

which also means  $[\text{A}^-]$  must be 0.00427. Since the acid is 0.1 M,  $[\text{HA}]$  must be  $(0.1 - 0.00427) = 0.99573$

Substituting these values in the Henderson-Hasselbalch equation gives us:

$$2.37 = \text{pK}_a + \log_{10}([\text{A}^-]/[\text{HA}])$$

$$2.37 = \text{pK}_a + \log_{10}(0.00427 / 0.99573)$$

$$2.37 = \text{pK}_a + \log_{10}(0.00429)$$

$$2.37 = \text{pK}_a + (-2.38)$$

$$4.75 = \text{pK}_a$$

Allowing for experimental and rounding errors, you might tentatively identify this acid as acetic acid, which has a  $\text{pK}_a$  of 4.76.

Q7: Knowing only the molarity and pH of an unknown acid solution, how might you identify the acid?

Calculate the  $\text{pK}_a$  for the unknown acid solution and compare the value you obtain with a list of the  $\text{pK}_a$  values for acids.

## Laboratory 11.2: Determine the pH of Aqueous Salt Solutions

Q1: What general conclusions can you draw from the pH values you observed for the four solutions?

A solution of a salt formed from a strong acid and a strong base (such as sodium chloride) or a weak acid and a weak base (such as ammonium acetate) has a pH near 7. A solution of a salt formed from a strong acid and a weak base (such as ammonium chloride) has an acidic pH. A solution of a salt formed from a weak acid and a strong base (such as sodium acetate) has a basic pH.

Q2: If you mixed equal amounts of a 0.1 M ammonium chloride solution and a 0.1 M sodium acetate solution, would you expect the pH of the resulting solution to be strongly acidic, weakly acidic, about neutral, weakly basic, or strongly basic? Why?

You would expect the pH to be about neutral, because the solution is formed from equal quantities of ammonium chloride, the salt of a strong acid and a weak base, and sodium acetate, the salt of a weak acid and a strong base.

### Laboratory 11.3: Observe the Characteristics of a Buffer Solution

Q1: How did the pH change compare in the buffer solution versus water?

In the buffer solution, pH changes very slowly as titrant is added. In water, the pH changes very quickly as even small amounts of titrant are added.

Q2: Calculate the expected pH of the buffer solution. How does the calculated value correspond to the observed value?

The concentrations of acetic acid and acetate ion are both 0.5 M. Substituting these concentrations in the Henderson-Hasselbalch equation gives us:

$$\text{pH} = \text{pK}_a + \log_{10}([\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}])$$

$$\text{pH} = \text{pK}_a + \log_{10}([0.5 \text{ mol/L}]/[0.5 \text{ mol/L}])$$

$$\text{pH} = \text{pK}_a + \log_{10}(1.0)$$

$$\text{pH} = \text{pK}_a + 0.0$$

The pH of this buffer solution is therefore equal to the  $\text{pK}_a$ , which is 4.76. The observed value should be close to 4.76.

Q3: Graph the amounts of added acid and base against the pH of the buffer solution. At what point does the buffer begin to lose effectiveness? Why?

The buffer solution maintains its pH close to nominal until the number of moles of added acid or base begins to approach the number of moles of acetic acid and acetate ion in the original buffer solution. At this point, the buffer is saturated because its equilibrium has been forced all the way to the left or to the right. That is, when all of the acetate ions have been forced to become molecular acetic acid, the buffer solution can no longer control the pH against the addition of acid, and when all of the molecular acetic acid has been forced to dissociate into acetate ions, the buffer solution can no longer control the pH against the addition of base. At or beyond either point, adding a small amount of a strong acid or strong base causes a rapid change in pH.

Q4: You have on hand 0.5 M solutions of acetic acid and sodium acetate. You want to make up 100 mL of a pH 5.0 buffer solution to calibrate your pH meter. Calculate the amounts of acetic acid solution and sodium acetate solution required to make up this buffer solution.

For a buffer made up with acetic acid and sodium acetate, the Henderson-Hasselbalch equation can be expressed as follows:

$$\text{pH} = \text{pK}_a + \log_{10}([\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}])$$

or, rearranging:

$$\text{pH} - \text{pK}_a = \log_{10}([\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}])$$

The required pH of the buffer solution and the  $\text{pK}_a$  of acetic acid are known, so we can simplify the equation to:

$$5.0 - 4.76 = 0.24 = \log_{10}([\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}])$$

or

$$1.7378 = ([\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}])$$

or

$$1.7378 * [\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$$

Since the ratio of acetic acid concentration to acetate ion concentration is 1.7378:1, the total volume of the solution is 2.7378, which equals 100 mL. Dividing 1.7378 by 2.7378 gives us the proportion of acetate ion in the final buffer solution:

$$1.7378 / 2.7378 = 0.6347$$

Multiplying that by the required 100 mL volume gives us the volume of sodium acetate solution required:

$$0.6347 * 100 \text{ mL} = 63.47 \text{ mL of sodium acetate solution}$$

$$100 \text{ mL} - 63.47 \text{ mL} = 36.53 \text{ mL of acetic acid solution}$$

## Laboratory 11.4: Standardize a Hydrochloric Acid Solution by Titration

Q1: Best practice when titrating an unknown is to do multiple titrations. Why?

The results from multiple titrations should be in very close agreement. If the results of the first two titrations differ significantly, it's likely that you made an error in one or the other (or both). Doing an additional titration or titrations and comparing the results with the first two runs tells you which results, if any, should be discarded. Furthermore, even if all of the runs have similar results, averaging those results gives a number that is more likely to be closer to the actual value.

Q2: List at least five possible sources of error in the procedure you followed in this laboratory.

Here are the most common sources of error:

- Chemical purity or concentration – If the actual purity or concentration of the stock chemicals you used in making up the initial solution differs from the values

stated on the label, your results will differ from the actual values. For example, a bottle of reagent-grade hydrochloric acid may state the contents as 37% but it's not uncommon for the actual concentration to range from 36% to 38%. Similarly, a bottle of reagent-grade anhydrous sodium carbonate may state the contents as 99.4% pure, but if that bottle had been opened previously the anhydrous sodium carbonate may have absorbed some water from the atmosphere, making the actual concentration of sodium carbonate by mass less than 99.4%.

- Mass or volume errors – any error in determining the mass or volume of the acids and bases you use to make up the initial solutions will obviously affect your results.
- Serial dilution errors – even people who are very careful in making up stock solutions for some reason are less careful in making serial dilutions. Perhaps the rationale is that the stuff is so dilute that it's not necessary to be as careful. Any error you making in doing the serial dilutions will affect the results.
- Titration errors – if you use your burette improperly or record the amount of titrant used improperly your results will differ from the actual values. The burette itself may also be inaccurate unless you have calibrated it properly.
- Observation errors – if you just read about doing titrations, you might believe that endpoints are always sharp and clear. In reality, the exact endpoint is often difficult to determine. You add that final partial drop of titrant, swirl the flask, and try to decide if the color change persists, but that pale color that was so obvious where the drop of titrant hit the solution is much less obvious when the solution is swirled. It's not uncommon for several titration runs to differ by a few drops or more due to observation errors. That's why it's a good idea to make multiple runs and average the results.
- Calculation errors – obviously, any calculation errors you make will affect the results.

Q3: You are titrating an unknown base solution and have standardized solutions of hydrochloric acid and acetic acid available. Is the acid you choose for the titration likely to affect the accuracy and/or precision of your results? If so, why?

Yes. The stronger acid (hydrochloric) is much more likely to provide an accurate result. The titration curves of strong acids (and bases) are nearly vertical near the end point, which is to say that adding a tiny amount of titrant causes a large change in pH. The titration curves of weak acids and bases show a much more gradual change in pH as titrant is added, which makes it more difficult to determine the end point with high accuracy or precision. Assuming proper procedures, titrating with a strong acid (or base) is likely to yield a repeatable values for the endpoint, while using a weak acid or base is likely to yield endpoints that differ significantly for multiple runs.

Q4: Other than using an indicator solution, how might you determine the equivalence point(s) for a titration?



First, obviously, you can use a pH meter rather than an indicator. Less obviously, there are many other techniques used to determine the endpoint, including:

- Potentiometric titrimetry – A potentiometer measures the electrode potential of a solution during a redox titration. At the endpoint, the potential of the working electrode changes suddenly and dramatically. A pH meter is a special type of potentiometer that is designed to measure specifically hydronium ions.
- Conductimetric titrimetry – the conductivity of an aqueous solution is determined by the type and concentration of the ions present. In an acid-base titration, for example, the solution has relatively high conductivity when hydronium or hydroxide ions are present in excess. At the endpoint, nearly all of the hydronium and hydroxide ions have combined to form neutral water molecules, so the conductivity of the solution reaches a sharp minimum.
- Amperometric titrimetry – in a redox titration, the current produced at a working electrode by the oxidation or reduction of reactants or products depends on the ion concentration of the species, and can be measured by an ammeter, which displays the endpoint as a sharp change in current.
- Calorimetric titrimetry – calorimetric titration measures the heat produced or consumed by a reaction to determine the endpoint.
- Thermometric titrimetry – thermometric titration measures the rate of the rise or fall in temperature (as opposed to heat produced or consumed, as with calorimetric titration). The rate of change is used to determine the endpoint of the titration.
- Spectroscopic titrimetry – a spectrometer can be used to measure the spectrum of the solution (using visible light, ultraviolet, or infrared) during titration if the spectrum of the reactant, titrant, or product is known by watching the relative concentrations.

In addition to these instrumental methods, either of two non-instrumental methods are commonly used if one or both is applicable to a particular titration reaction:

- Color change – in some reactions, the reactants are colorless and the product colored, or vice versa. In such reactions, the reaction itself serves as its own indicator. This method is most often used with redox titrations in which different oxidation states of the species in question have significantly different colors.
- Precipitation – if the reaction forms an insoluble solid, that solid precipitates as titrant is added and the precipitation ceases at the end point. In practice, it's usually very difficult to determine the end point by precipitation alone because enough of the precipitate usually remains suspended to make it difficult to determine when precipitation has ceased.

## Chapter 12 – Chemical Kinetics

### Laboratory 12.1: Determine the Effect of Temperature on Reaction Rate

Q1: What effect did you observe temperature to have on reaction rate?

Reaction rate increases with increasing temperature.

Q2: Based on the data you recorded in Table 12-1, does the 10 °C rule of thumb provide a reasonably close approximation of the observed reaction rates in this laboratory? How far do your data depart from the expected values based on the rule of thumb?

Answers will vary, depending on experimental conditions, the type of fizzy tablets used, and so on. However, experimental results should indicate an approximate doubling of reaction rate with each 10 °C increase in temperature.

Q3: Based on the data you recorded in Table 12-1, does reaction rate appear to be approximately linear over time? If you noticed an increase or decrease in reaction rate over time, propose at least one possible explanation.

In our trial runs, once the reaction had begun the reaction rate as measured by mass loss was reasonably linear during the early stages of the reaction. As the reaction progressed, the reaction rate (again, as measured by mass loss) began to fall. Because there was a large excess of water in the cup relative to the mass of the fizzy tablet, the only real variables that might explain this falloff in reaction rate are the decreasing size and mass of the tablet.

The most reasonable explanation for the decrease in reaction rate late in the reaction is that as the tablet got smaller, its surface area decreased. With less surface area available for the reaction to take place, it's reasonable to assume that the overall rate of reaction would decrease.

Note that we calculated absolute mass loss based on the original mass of the tablet. It would be interesting to calculate relative mass loss at each interval, using the remaining mass of the tablet at the beginning of that interval.

### Laboratory 12.2: Determine the Effect of Surface Area on Reaction Rate

Q1: What effect did you observe surface area to have on reaction rate?

Reaction rate increases as surface area increases.

Q2: Use the ruler to measure the diameter and thickness of a tablet. Calculate its approximate surface area. Make the same calculation for surface area of the quartered tablet. Does the increase in reaction rate you observed with the quartered tablet approximately correspond to the increase in surface area? If not, propose an explanation.

Answers will vary, but the initial reaction rate should increase approximately proportionately to the increased surface area of the tablet.

Q3: Most fizzy tablet remedies direct the user to dissolve two tablets in a glass of water. Why don't they simply make the tablets larger and recommend dissolving only one of the larger tablets?

One large fizzy tablet would take longer to dissolve than the same mass of medication in two smaller tablets.

### **Laboratory 12.3: Determine the Effect of Concentration on Reaction Rate**

Q1: What effect did you observe concentration to have on reaction rate?

Reaction rate increases as concentration increases.

Q2: Based on the data you recorded in Table 12-3, is the effect of concentration on reaction rate linear?

Answers may vary depending on reaction conditions and the type of tablet used, but in our trial runs the effect of concentration on reaction rate was reasonably linear, taking into account the reduction in surface area mentioned in the answer to question 3 in Laboratory 12.1.

Q3: Based on the data you recorded in Table 12-3, at any particular concentration does reaction rate appear to be approximately linear over time? If you noticed an increase or decrease in reaction rate over time, propose at least one possible explanation.

Answers may vary, but in our trial runs the reaction rates were relatively linear over time with the 4 M and 2 M concentrations, taking into account the slowing of reaction rate late in the reaction, which is discussed above. The trial run with 1 M hydrochloric acid showed a slightly steeper falloff in reaction rate late in the reaction.

One likely explanation is that 100 mL of 1 M HCl contains 0.1 mole of HCl, while the tablet we used contained 750 mg (~0.0075 moles) of calcium carbonate. Hydrochloric acid and calcium carbonate react in the mole ratio of 2:1, so that tablet consumed about 0.015 moles of hydrochloric acid, reducing the concentration of the acid from 1.0 M initially to 0.85 M when the reaction completed. This reduction in concentration helps explain the faster falloff in reaction rate we observed late in the reaction with the 1 M HCl.

### **Laboratory 12.4: Determine the Effect of a Catalyst on Reaction Rate**

Q1: What effect did you observe the catalase catalyst to have on reaction rate?

The presence of the catalase catalyst increased the reaction rate dramatically.

Q2: Based on the data you recorded in Table 12-4, is the effect of the catalyst on reaction rate linear? If not, propose an explanation.

Answers will vary—the most significant factor is the actual concentration of the catalase enzyme—but in our trial runs the reaction rate was reasonably linear through 60 seconds, tailing off slightly at 120 seconds, and more noticeably at 240 seconds.

Q3: Would you expect the reaction rate to increase, decrease, or remain the same if you increased the amount of catalyst? Why?

Within reason, the reaction rate increases as you increase the amount of catalyst. We mentioned in the introduction to this lab session that one catalase molecule catalyzes the reaction of millions of peroxide molecules per second. Although the exact rate varies with temperature, peroxide concentration, and other factors, we can assume that that rate is fixed for the purposes of this lab session. That means that for any particular concentration of catalase, doubling the concentration essentially doubles the reaction rate.

Q4: When you begin a titration of a reacted hydrogen peroxide solution, you find that the first drop of potassium permanganate titrant causes the solution to assume a purple color. What has happened?

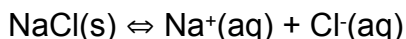
All of the hydrogen peroxide initially present in that solution has reacted to form oxygen and water. Because no peroxide remains in solution to react with the permanganate ions, the first drop of titrant has nothing to react with and so gives the solution a purple color.

## Chapter 13 – Chemical Equilibrium and Le Chatelier's Principle

### Laboratory 13.1: Observe Le Chatelier's Principle in Action

Q1: In Part I, what substance was formed as you added concentrated hydrochloric acid to the saturated solution of sodium chloride? Why?

A fine precipitate of solid sodium chloride. In a saturated solution of sodium chloride, solid sodium chloride is in equilibrium with dissociated sodium ions and chloride ions, according to the following equilibrium equation:



Adding concentrated hydrochloric acid increases the concentration of chloride ions, forcing the equilibrium to the left.

Q2: In Part I, what substance was formed as you added saturated sodium carbonate solution to the saturated solution of sodium chloride? Why?

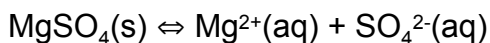
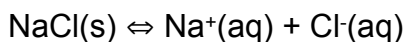
The simple answer is that a precipitate of a solid sodium salt occurs because the addition of sodium ions forces the equilibrium to the left. The real answer is that sodium chloride, sodium carbonate, or a mixture of both may precipitate, with the exact makeup of the precipitate dependent on the temperature of the solution and the initial concentration of the sodium carbonate and sodium chloride solutions, which vary with temperature.

The solubility of sodium chloride is similar across a wide range of temperatures. For example, at 0 °C, 100 mL of water dissolves 35.7 g of sodium chloride, versus 36.4 g at 40 °C. The solubility of sodium carbonate varies much more with temperature. For example, at 0 °C, 100 mL of water dissolves only 7.0 g of sodium carbonate, versus 49.0 g at 40 °C.

To further complicate matters, those solubilities are listed for pure water, when what we really need to calculate relative solubilities are the solubility constants for sodium carbonate in a saturated solution of sodium chloride and for sodium chloride in a saturated solution of sodium carbonate.

Q3: In Part I, explain what occurred when you added the saturated magnesium sulfate solution.

In our trial run, the solution remained clear. The two equilibrium equations are:



Adding the magnesium sulfate solution to the saturated solution of sodium chloride added neither sodium ions nor chloride ions, so the sodium chloride equilibrium equation is unaffected. (Note that under some conditions, adding foreign ions to a saturated solution can force the equilibrium to change even

though the added ions are of different species because the total ionic concentration of the solution changes.)

Q4: If you repeated Part I in a pressure chamber at 10 atmospheres, would you expect different results? Why or why not?

You would expect the same results. Although pressure can affect equilibrium by changing volume, water is essentially incompressible, so any volume change from a mere 10 atmosphere increase in pressure is vanishingly small.

Q5: In Part II, we observed the qualitative effect of temperature on the dynamic equilibrium of a saturated sodium chloride solution. If you were charged with designing an experiment to obtain quantitative data, how would you proceed?

One possible procedure is as follows:

- Transfer about 20 mL of water to a test tube and sufficient sodium chloride to produce a saturated solution with solid sodium chloride remaining on the bottom of the test tube.
- Cool the test tube to 0 °C and allow the solution to reach equilibrium, ensuring that solid sodium chloride remains in the test tube.
- Use a pipette to transfer 10.00 mL of solution from the test tube to a dry, weighed evaporating dish. Allow the water to evaporate and determine the mass of sodium chloride contained in 10.00 mL of solution at 0 °C.
- Repeat these steps for saturated sodium chloride solutions at other temperatures.

Q6: In Part III, we observed the effect of increasing the volume of solvent on the dynamic equilibrium of a saturated sodium chloride solution. Is it possible that, for some compounds, increasing the volume of solvent would reduce the amount of solute that dissolved? Why or why not?

No, it is not possible. For a larger volume of solvent to dissolve less of a solute, the solute would have to have negative solubility in that solvent (a negative solubility constant), which is impossible.

Q7: In Part IV, we observed the effect of pressure on the dynamic equilibrium of a carbonated soft drink at two different temperatures. The differing results at the two temperatures illustrate the concept of *retrograde solubility*, which is the chemist's way of referring to a compound that is less soluble at higher temperature. What mechanism explains the lower solubility of carbon dioxide gas in water at higher temperatures?

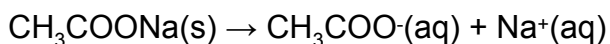
Molecules are constantly in motion at any temperature above absolute zero. As the temperature of the aqueous solution of carbon dioxide increases, the average speed of the carbon dioxide molecules in the solution also increases. At higher speed, a larger percentage of the carbon dioxide molecules have sufficient energy to break the attractive forces that hold them in solution, which is another way of saying that as the temperature of the solution increases, the partial pressure of the carbon dioxide also increases.

## Laboratory 13.2: Quantify the Common Ion Effect

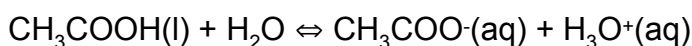
Q1: What effect does a higher concentration of sodium acetate have on the pH of solution after the acetic acid has been added? Propose an explanation based on your understanding of Le Chatelier's principle.

The higher the concentration of sodium acetate, the higher the pH.

Sodium acetate is an ionic compound that dissociates essentially completely in aqueous solution, yielding sodium ( $\text{Na}^+$ ) ions and acetate ( $\text{CH}_3\text{COO}^-$ ) ions.



Acetic acid is a weak acid that dissociates only partially in solution to yield solvated hydrogen ions ( $\text{H}_3\text{O}^+$ ) and acetate ions.



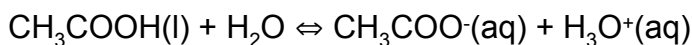
The presence of acetate ions from dissolved sodium acetate forces this equilibrium to the left, increasing the amount of acetic acid present in molecular form, and reducing the amount present in dissociated form. Reducing the amount of acetic acid in dissociated form reduces  $\text{H}_3\text{O}^+$  concentration, increasing the pH.

Q2: Do the pH values of the various samples change after 15 minutes and/or 60 minutes? Why or why not?

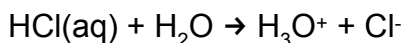
If you mixed the acetic acid into the sodium acetate solution thoroughly before measuring the pH, there should be no change. At room temperature, the solution of sodium acetate and acetic acid reaches a new equilibrium quickly. Once it achieves equilibrium, no further changes occur over time unless you make another change to the reaction environment.

Q3: If you repeated this experiment, substituting sodium chloride for sodium acetate and concentrated hydrochloric acid for acetic acid, would you expect the pH changes in different concentrations of sodium chloride solution to be greater than or less than the corresponding changes in the sodium acetate solution. Why?

You would expect any pH changes to be smaller (probably not measurable with home lab equipment). The difference is that acetic acid is a weak acid, and so dissociates only partially in aqueous solution.



Hydrochloric acid, conversely, is a very strong acid, which dissociates almost entirely in aqueous solution.



This reaction proceeds spontaneously to completion, with all of the molecular HCl reactant converted to hydronium ion and chloride ion products. Adding chloride ions does almost nothing to force the equilibrium to the left, so the hydronium ion concentration (and therefore the pH) remains nearly constant.

### Laboratory 13.3: Determine a Solubility Product Constant

Q1: Why did we record the temperatures of the saturated solutions?

The solubility of compounds, including those that are nearly insoluble, varies with temperature.

Q2: The solubility of silver chromate,  $\text{Ag}_2\text{CrO}_4$ , is  $6.5 \cdot 10^{-5}$  mol/L. What is the  $K_{\text{sp}}$  of silver chromate?

The  $K_{\text{sp}}$  of silver chromate is  $1.1 \cdot 10^{-12}$ , determined as follows:

The solubility product constant for silver chromate can be expressed as:

$$K_{\text{sp}} = [\text{Ag}^+]^2 \cdot [\text{Cr}_2\text{O}_4^{2-}]$$

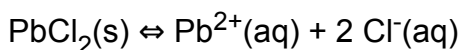
The concentration of the chromate ion is  $6.5 \cdot 10^{-5}$  mol/L. The concentration of the silver ion is twice that value, or  $1.3 \cdot 10^{-4}$  mol/L. Substituting those values:

$$K_{\text{sp}} = (1.3 \cdot 10^{-4})^2 \cdot (6.5 \cdot 10^{-5}) = 1.1 \cdot 10^{-12}$$

Q3: The  $K_{\text{sp}}$  of lead chloride ( $\text{PbCl}_2$ ) is  $1.6 \cdot 10^{-5}$ . What is solubility of lead chloride in g/L?

The solubility of lead chloride is 4.4 g/L, determined as follows:

The equilibrium expression is:



From this, we can state the  $K_{\text{sp}}$  equation as:

$$K_{\text{sp}} = 1.6 \cdot 10^{-5} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$

In solution, the concentration of the chloride ion is twice the concentration of the lead ion. If we designate the concentration of the lead ion as  $x$ , the equation becomes:

$$1.6 \cdot 10^{-5} = (x) \cdot (2x)^2$$

$$1.6 \cdot 10^{-5} = 4x^3$$

$$4.0 \cdot 10^{-6} = x^3$$

$$1.6 \cdot 10^{-2} = x = 0.016$$

so a saturated solution of lead chloride is 0.016 M.

The gram molecular mass of lead chloride is 278.1 g/mol, so

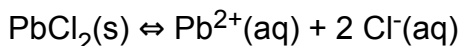
$$(0.016 \text{ mol/L}) \cdot (278.1 \text{ g/mol}) = 4.4 \text{ g/L}$$

Q4: What is solubility of lead chloride in mol/L in 0.1 M hydrochloric acid? (Assume the HCL is fully dissociated.)



The solubility of lead chloride in mol/L in 0.1 M hydrochloric acid is 0.0016 mol/L, determined as follows:

Again, the equilibrium expression is:



and from this we can state the  $K_{\text{sp}}$  equation as:

$$K_{\text{sp}} = 1.6 \cdot 10^{-5} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$

In this case, however, the lead chloride is not the only source of chloride ion. The 0.1 M solution of hydrochloric acid, which we assume is fully dissociated, provides an initial chloride ion concentration of 0.1 M.

Once again, we designate the concentration of the lead ion as  $x$ , which makes the chloride ion concentration  $2x + 0.1$  (the chloride ion concentration from the dissociated lead chloride + the 0.1 M concentration provided by the HCl).

Substituting these values:

$$1.6 \cdot 10^{-5} = (x) \cdot (2x + 0.1)^2$$

We could expand and solve the quadratic equation or use successive approximations to solve for  $x$ , but in practice there's no benefit to doing that because the "improved" accuracy of our estimate will be lost in the significant figures.

We know that the solubility of lead chloride in pure water is very low and that the common ion effect will greatly reduce the solubility of lead chloride in HCl, so we'll make the simplifying assumption that  $x$  will be a very small value, so in effect all of the chloride ion in solution is from the dissociation of HCl. That simplifies the equation to:

$$1.6 \cdot 10^{-5} = (x) \cdot (0.1)^2$$

$$1.6 \cdot 10^{-3} = x = 0.0016 \text{ mol/L}$$

To check our assumption, we substitute this value in the  $K_{\text{sp}}$  equation:

$$K_{\text{sp}} = (x) \cdot (2x + 0.1)^2$$

$$K_{\text{sp}} = (1.6 \cdot 10^{-3}) \cdot (3.2 \cdot 10^{-3} + 1 \cdot 10^{-1})^2$$

$$K_{\text{sp}} = 1.7 \cdot 10^{-5}$$

That value corresponds quite closely to the actual value of  $K_{\text{sp}} = 1.6 \cdot 10^{-5}$ , so our simplifying assumption was valid. (The actual value for molar solubility obtained by solving the quadratic equation is 0.0015 mol/L.)

## Chapter 14 – Gas Chemistry

### Laboratory 14.1: Observe the Volume-Pressure Relationship of Gases (Boyle's Law)

Q1: Graph pressure (x-axis) versus volume (y-axis) using your observed and calculated (predicted) volumes? What general form do the graphs take (linear, exponential, etc.)? How closely do your observed values correspond to your calculated values?

Answers will vary depending on experimental results, but the graphs should be approximately linear and the observed values should be reasonably close to calculated values.

Q2: Calculate percent error for your observed data. What experimental errors might explain the differences between the observed and calculated values?

Answers will vary. Here are some of the most common reasons for error:

- Binding in the syringe. Even a well-lubricated plunger has some friction.
- Errors in measuring the bore of the syringe and/or in calculating its area.
- Errors in reading the initial and/or final volume of the syringe.
- Using an incorrect atmospheric pressure, or not taking it into account.
- Errors in determining the mass pressing on the syringe plunger, including failing to take into account the mass of the container and/or plunger.

Q3: Could you use this apparatus to determine the mass of an unknown sample? If so, how would you go about determining the mass?

Set up the apparatus and record the volume reading with only atmospheric pressure and the mass of the plunger and container acting on the gas within the syringe. Add the unknown sample to the container and record the new volume reading. Apply Boyle's Law,  $V_1 \cdot P_1 = V_2 \cdot P_2$ , to determine the final pressure ( $P_2$ ) exerted by atmospheric pressure, the mass of the plunger, container, and sample. Subtract the initial pressure,  $P_1$ , from the final pressure,  $P_2$ , to determine the difference in pressure. Using the bore area of the syringe, calculate the mass required to exert that additional pressure.

Q4: The initial pressure in a Boyle's Law apparatus is known to be 29,084 Pa and the initial volume 10.0 mL. Assuming a perfect apparatus (no friction, etc.) how much total pressure must be applied to reduce the volume to 5.0 mL?

Apply Boyle's Law,  $V_1 \cdot P_1 = V_2 \cdot P_2$

$$10.0 \text{ mL} \cdot 29,084 \text{ Pa} = 5.0 \text{ mL} \cdot P_2$$

$$(10.0 \text{ mL} \cdot 29,084 \text{ Pa}) / 5.0 \text{ mL} = P_2$$

$$58,168 \text{ Pa} = P_2$$

## Laboratory 14.2: Observe the Volume-Temperature Relationship of Gases (Charles's Law)

Q1: Graph kelvin temperature (x-axis) versus volume (y-axis) using your observed and calculated (predicted) volumes? What general form do the graphs take (linear, exponential, etc.)? How closely do your observed values correspond to your calculated values?

Answers will vary depending on experimental results, but the graphs should be approximately linear and the observed values should be reasonably close to calculated values.

Q2: What volume would your gas sample have if you were able to cool it to absolute zero? Extrapolate your experimental data to estimate the kelvin temperature of absolute zero? How closely does your extrapolation correspond to the actual temperature of absolute zero (0 K)?

Apply Charles's Law,  $V_1 \cdot T_2 = V_2 \cdot T_1$

For any arbitrary value for initial volume ( $V_1$ ), the final temperature ( $T_2$ ) is 0K, which makes the product of the left side of the equation 0. Therefore, for any arbitrary non-zero value for the initial temperature ( $T_1$ ), the final volume ( $V_2$ ) must be zero for the equation to balance. Therefore, the volume of the gas sample at 0K must be 0. (Obviously, any real gas sample would have a small but finite volume at 0K, but conventionally the volume at 0K is assumed to be 0.)

The extrapolated value for absolute zero, where the line crosses the axis at zero volume, should be reasonably close to 0K.

Q3: A sample of gas has a volume of 10.00 mL at 26.85 °C. With pressure held constant, what volume would that sample occupy at -173.15 °C? At 126.85 °C?

Apply Charles's Law,  $V_1 \cdot T_2 = V_2 \cdot T_1$ , after converting the Celsius temperatures to kelvins.

At -173.15 °C:

$$10.00 \text{ mL} \cdot 100 \text{ K} = V_2 \cdot 300 \text{ K}$$

$$(10.00 \text{ mL} \cdot 100 \text{ K}) / 300 \text{ K} = V_2 = 3.33 \text{ mL}$$

At 126.85 °C:

$$10.00 \text{ mL} \cdot 400 \text{ K} = V_2 \cdot 300 \text{ K}$$

$$(10.00 \text{ mL} \cdot 400 \text{ K}) / 300 \text{ K} = V_2 = 13.33 \text{ mL}$$

Q4: A sample of gas has a volume of 10.00 mL at 26.85 °C. With pressure held constant, at what temperature would that sample occupy 15.00 mL?

Apply Charles's Law,  $V_1 \cdot T_2 = V_2 \cdot T_1$ , after converting the Celsius temperature to kelvins.

$$10.00 \text{ mL} \cdot T_2 = 15.00 \text{ mL} \cdot 300 \text{ K}$$

$$T_2 = (15.00 \text{ mL} \cdot 300 \text{ K}) / 10.00 \text{ mL} = 450 \text{ K}$$

To convert kelvins to °C:

$$450 \text{ K} - 273.15 = 176.85 \text{ °C}$$

### Laboratory 14.3: Observe the Pressure-Temperature Relationship of Gases (Gay-Lussac's Law)

Q1 A gas sample at a pressure of 101,325 Pa and 26.85 °C has a volume of 10.00 mL. At constant volume, at what pressure would that gas sample have a temperature of 126.85 °C?

Apply Gay-Lussac's Law,  $P_1 \cdot T_2 = P_2 \cdot T_1$ , after converting the Celsius temperature to kelvins.

$$101,325 \text{ Pa} \cdot 400 \text{ K} = P_2 \cdot 300 \text{ K}$$

$$(101,325 \text{ Pa} \cdot 400 \text{ K}) / 300 \text{ K} = P_2 = 135,100 \text{ Pa}$$

Q2: A sample of gas at a pressure of 101,325 Pa and 26.85 °C has a volume of 10.00 mL. If the temperature is increased to 126.85 °C and the volume decreased to 5.00 mL, what is the pressure of the gas sample?

To begin, apply Gay-Lussac's Law,  $P_1 \cdot T_2 = P_2 \cdot T_1$ , after converting the Celsius temperatures to kelvins.

$$101,325 \text{ Pa} \cdot 400 \text{ K} = P_2 \cdot 300 \text{ K}$$

$$(101,325 \text{ Pa} \cdot 400 \text{ K}) / 300 \text{ K} = P_2 = 135,100 \text{ Pa}$$

which gives us the pressure at 400 K (126.85 °C) with the volume constant at 10.00 mL. Use this value as the initial value for the Boyle's Law equation:

$$V_1 \cdot P_1 = V_2 \cdot P_2$$

$$10.00 \text{ mL} \cdot 135,100 \text{ PA} = 5.00 \text{ mL} \cdot P_2 =$$

$$(10.00 \text{ mL} \cdot 135,100 \text{ PA}) / 5.00 \text{ mL} = P_2 = 270,200 \text{ Pa}$$

### Laboratory 14.4: Use the Ideal Gas Law to Determine the Percentage of Acetic Acid in Vinegar

Q1: If a reaction between acetic acid and sodium hydrogen carbonate produces 1.585 liters of carbon dioxide gas at a temperature of 297.0 K and a pressure of 100.000 kPa, how many moles of carbon dioxide were produced?

Apply the Ideal Gas Law,  $PV = nRT$ , where P is absolute pressure, V is volume, n is the number of moles, R is the ideal gas constant, and T is the temperature in kelvins. For volume stated in liters and pressure in kPa, the value of the ideal gas constant is  $8.314472 \text{ L} \cdot \text{kPa} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ .

$$PV = nRT$$

$$n = (PV / RT)$$

$$n = (100.000 \text{ kPa} \cdot 1.585 \text{ L}) / (8.314472 \text{ L} \cdot \text{kPa} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 297.0 \text{ K})$$

$$n = 0.0642 \text{ mol}$$

Q2: Use the ideal gas law to determine how many liters one mole of gas occupies at a temperature of 273.15 K and a pressure of 101.325 kPa.

$$PV = nRT$$

$$V = (nRT)/P$$

$$V = (1 \text{ mol} \cdot 8.314472 \text{ L} \cdot \text{kPa} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 273.15 \text{ K}) / 101.325 \text{ kPa}$$

$$V = 22.414 \text{ L}$$

### Laboratory 14.5: Determine Molar Mass from Vapor Density

Q1: The actual molar mass of acetone is 58.09 g/mol. How closely did your experimental result correspond to the actual value? Propose at least two possible explanations for any variation in your result.

Answers will vary, but should be reasonably close to the actual value. Here are several possible sources of experimental error:

- An error in determining the initial and/or final mass of the reaction apparatus causes the experimental value to be higher or lower than the actual value, depending on the direction of the mass error.
- Using too large a hole in the aluminum foil cap, which allows air to mix with the acetone vapor inside the flask. Because the vapor inside the flask is then a mixture of air and acetone rather than pure acetone, the mass of the condensed acetone will be smaller than it should be, yielding an experimental molar mass lower than the actual value.
- Allowing some acetone to remain in liquid form means that the mass you determine for the acetone vapor will also include the mass of the unvaporized acetone, leading to a higher than actual value for molar mass.
- Heating the vapor in the flask above the boiling point causes the pressure of the vapor to increase above atmospheric pressure, forcing some acetone vapor out of the flask. When the remaining vapor condenses, there will be less liquid acetone than there would have been if the acetone vapor had been maintained at atmospheric pressure, leading to a lower than actual value for molar mass.
- Errors in determining the volume of the flask cause the experimental value for molar mass to be larger or smaller than the actual value, depending on the direction of the volume error.
- Failing to dry the outside of the flask completely adds the mass of any water adhering to the flask to the mass of condensed acetone vapor, leading to a higher than actual value for molar mass.

Q2: Could this method be used unmodified to determine the molar mass of trichloroacetic acid? If not, why not, and what modification to the apparatus would be required to determine the molar mass of trichloroacetic acid?

No, because the boiling point of trichloroacetic acid is 196 °C, which is higher than the boiling point of water. You could modify the water bath to use a liquid such as mineral oil that has a boiling point higher than 196 °C.

Q3: At 25°C, the vapor pressure of acetone is about 26.67 kilopascals. Can this information be used to increase the accuracy of your calculated molar mass of acetone? If so, how?

Yes. We made some assumptions in doing this experiment. The initial mass of the flask included the actual mass of the flask itself plus the mass of air it contains. When we boil the acetone to fill the flask with acetone vapor and then condense that vapor to liquid, we make two assumptions:

- that the volume of air in the flask after condensing the will be the same as the initial volume of air. Obviously, that's not true, because the liquid acetone occupies some small part of the total volume of the flask.
- We assume that all of the acetone vapor is condensed to liquid acetone and that pure air fills the remaining volume of the flask. That assumption introduces another error, because the "air" is actually a mix of air and acetone vapor. (The stated vapor pressure of acetone, 26.67 kPa, means that the partial pressure of acetone makes up about one quarter of the total pressure.)

We could improve the accuracy of our calculation of the molar mass of acetone by taking these factors into account.

Q4: What modifications could you make to this procedure to reduce experimental error?

Any modifications that would reduce or eliminate any of the errors listed in Q1.

Q5: Propose a method using only the standard laboratory equipment listed in Chapter 3 for determining the molar mass of carbon dioxide gas. What change to your proposed method would you make if you had a vacuum pump available?

Choose a one-hole rubber stopper that fits a flask. Glue or otherwise secure a piece of aluminum foil to the stopper, and make a pinhole in the aluminum foil. Seat the stopper fully in the flask and mark the level of the bottom of the stopper with a glass marking pen or by applying a sticky label to the outside of the flask. Determine the mass of this apparatus as accurately as possible and record it.

Fill the flask with carbon dioxide by adding a few chunks of dry ice to the flask and stoppering the flask with the stopper seated to the marked level. Determine the mass of the flask when filled with carbon dioxide as accurately as possible, and record it.

Remove the stopper from the flask and fill the flask with water to the level marked by the line or label. Determine the mass of the flask filled with water as accurately as possible, and record it. Measure the temperature of the water, look

up the density of water at that temperature, and use that value to determine the volume of the flask to the marked line.

At this point, we know the volume of the flask and the masses of the flask when filled with air and when filled with carbon dioxide. In order to determine the actual mass of the carbon dioxide contained in that volume, we need to determine the mass of the air. At 25 °C, the density of dry air is 1.185 g/L. Using this value and the volume of the flask, you can determine the mass of air contained in the flask, and subtract that from the initial mass of the “empty” flask. Subtracting that value from the mass of the flask when filled with carbon dioxide gives you the mass of the carbon dioxide contained in the known volume of the flask. From that value, the molar mass of carbon dioxide can be calculated.

If you had a vacuum pump available, you would use it to evacuate all of the air from the flask before determining its initial mass. By doing so, you would eliminate the mass of the air contained in the flask as an unknown, and you could simply subtract the mass of the evacuated flask from the mass of the flask when filled with carbon dioxide gas at atmospheric pressure to determine the molar mass of carbon dioxide.

Q6: If your sample had been unknown, would you have been able to identify the substance from the molar mass you determined experimentally? What other datum you obtained could be used to confirm the identity of the sample?

Answers will vary, depending on how closely the experimental value for molar mass corresponds to the actual value. The identity of the unknown can be narrowed down by comparing the experimentally-determined molar mass to a table of known molar masses for various compounds.

Although many compounds may have molar masses similar to the value we obtained experimentally, their boiling points often differ significantly. Because we determined the boiling point of our sample, that in combination with the molar mass value we obtained should be sufficient to identify the sample if it were unknown.

## Chapter 15 – Thermochemistry and Calorimetry

### Laboratory 15.1: Determine Heat of Solution

Q1: Using your experimental data, calculate the heats of solution for ammonium nitrate, sodium chloride, and sodium hydroxide. Enter your calculated values in Table 15-1.

Answers will vary.

Q2: Look up published values for the heats of solution of those three compounds on the Internet or in a printed reference. How closely do the values you obtained experimentally correspond to the published values? If your values are significantly different, propose possible explanations.

Answers will vary, but should be reasonably close to these values from the CRC handbook:

Ammonium nitrate: +25.69 kJ/mol (+6.14 C/mol)

Sodium chloride: +3.88 kJ/mol (+0.93 C/mol)

Sodium hydroxide: -44.51 kJ/mol (-10.64 C/mol)

The most likely types of experimental error are mistakes in determining the mass of the water and salts, using an inaccurate or uncalibrated thermometer, and calculating the heats of solution based only on the mass of the water (rather than including the masses of the dissolved salts).

For the most accurate results, the thermal mass of the calorimeter itself must be taken into account, but the thermal mass of either the home made or commercial calorimeter we use is much smaller than the mass of the water and salts used.

### Laboratory 15.2: Determine the Specific Heat of Ice

Q1: Using your experimental data for each of the first two trials, calculate the heat of fusion of ice in cal/g and record your calculated values on Line G of Table 15-2. The actual value for the heat of fusion of ice is 79.72 cal/g. If the value you obtained experimentally differs significantly, propose possible reasons for this variation.

Answers will vary, but should be at least moderately close to the actual value.

This is a “sloppy” experiment, in that it's almost impossible to have anything other than a mixture of water and ice at each stage. The ice you add to the calorimeter actually contains some liquid water, and the strained ice after the reaction also retains some liquid water. (We hope those errors offset each other, which they largely do.)

Other possible reasons for variations are errors in measuring or recording the initial or final volume of the water, errors in measuring or recording the temperature, an inaccurate or uncalibrated thermometer, or using ice at a temperature other than 0 °C.



### Laboratory 15.3: Determine the Specific Heat of a Metal

Q1: Using your experimental data for the lead shot and iron shot, calculate the specific heat of lead and iron in J/g·°C and record your calculated values on Line G of Table 15-3.

Answers will vary.

Q2: The actual values for the specific heat of lead and iron are 0.127 J/g·°C and 0.450 J/g·°C, respectively. Calculate the percent error of the value you obtained experimentally.

Answers will vary, but should be reasonably close to the actual values.

Q3: Propose several possible explanations for experimental error.

The most likely experimental errors are:

- errors in determining or recording the mass of lead or iron shot.
- errors in determining or recording the volume (and mass) of the water used.
- errors in determining or recording the temperature of the water.
- not allowing sufficient time for the shot to equilibrate with the water bath.

Q4: After completing this laboratory, a student learned that her digital thermometer consistently reads 0.8 °C high. What effect did this error have on the specific heat values she determined experimentally? Why?

None. The actual temperature is not used in calculating the specific heat of the samples, so it is immaterial. Only the *change* in temperature matters, and because the thermometer consistently reads 0.8 °C high, the values this student recorded for the change in temperature are accurate.

Q5: After completing this laboratory, a student learned that his graduated cylinder consistently delivered 5% less liquid than indicated. What effect did this error have on the specific heat values he determined experimentally? Why?

Assuming no other errors, the values this student obtains for specific heat will be about 5.3% higher than the actual values.

$$c_{\text{metal}} = (mc\Delta T)_{\text{water}} / -(m\Delta T)_{\text{metal}}$$

If the volume (and therefore mass) of the water is 5% smaller than assumed, the calculated value for  $c$  will be

$$100/95 = 1.053$$

times the actual value.

### Laboratory 15.4: Determine the Enthalpy Change of a Reaction

Q1: Calculate the heat of reaction and enter the value on Line G of Table 15-4. (Hint: remember to use the proper sign.)

Answers will vary.

Q2: Calculate the number of moles of sodium hydroxide that reacted and enter that value on Line H of Table 15-4.

Answers will vary.

Q3: Calculate the enthalpy change of reaction and enter that value on Line I of table 15-4.

Answers will vary.

Q4: Using the known value for enthalpy of reaction, calculate the percent error in your experimental results. (Use the proper sign.)

Answers will vary.

Q5: Propose several possible reasons for the experimental error you calculated in the preceding question.

The most likely experimental errors are:

- inaccurate molarities for the sodium hydroxide and/or hydrochloric acid solutions.
- errors in determining or recording the volumes of the solutions.
- errors in determining or recording the temperatures of the solutions.
- not allowing sufficient time for the reaction to complete.

## Chapter 16 – Electrochemistry

### Laboratory 16.1: Produce Hydrogen and Oxygen by Electrolysis of Water

Q1: From looking at the balanced equation and your own observations during this lab, which gas was produced at the anode and which at the cathode? What evidence supports your conclusions?

Oxygen is produced at the anode and hydrogen gas at the cathode.

We know that electrolysis splits two molecules of water into one molecule of oxygen gas and two molecules of hydrogen gas. We observe that gas accumulates in the test tube over the cathode about twice as fast as in the test tube over the anode, so that must mean that hydrogen gas is evolved at the cathode.

We could further confirm this conclusion by testing the gas in each test tube with a burning splint. Hydrogen gas explodes with a soft pop, while oxygen gas causes the splint to burn fiercely.

Q2: Using the values you recorded on Lines F and G of Table 16-1, calculate the volume ratio of the two gases produced and the percentage error from the theoretical yield.

Answers will vary, but should be quite close to the theoretical 2:1 ratio of hydrogen to oxygen.

Q3: Comparing your observations for igniting the cathode gas versus igniting the mixed cathode and anode gases, why was the combustion of the mixed gases so much more vigorous?

Hydrogen (the cathode gas) burns in air by combining with atmospheric oxygen to form water. The atmosphere contains less than 20% oxygen, while the anode gas is pure oxygen. The volumes of gases in the two test tubes are by definition present in stoichiometric balance, so each oxygen molecule has available exactly the two hydrogen molecules with which it can react to form water. This is the ideal mixture for combustion—neither gas is present in excess and no other gases are present—so the reaction is extremely vigorous.

Q4: At standard temperature and pressure, one mole of a gas occupies about 22.4 L. The density of water is 1.00 g/mL and its formula weight is 18.02 g/mol. If your test tube of mixed anode and cathode gases contains a total of 25.0 mL of gases in a 2:1 hydrogen:oxygen ratio, how much liquid water is produced when they combust?

The 25.0 mL of mixed gases contain hydrogen and oxygen in the mole ratio of 2:1, which is stoichiometrically balanced. That sample contains 8.33 mL of oxygen, so we can calculate the number of moles of oxygen present:

$$8.33 \text{ mL} / (22,400 \text{ mL/mol}) = 0.000372 \text{ mol}$$

Since one mole of oxygen reacts with hydrogen to form one mole of water, we can calculate the mass of water produced by the reaction:

$$0.000372 \text{ mol} \times 18.02 \text{ g/mol} = 0.00670 \text{ g}$$

We're using a value of 1.00 g/mL for the density of water, which means the reaction produces 0.00670 mL of water.

## Laboratory 16.2: Observe the Electrochemical Oxidation of Iron

Q1: Which of the nails showed the greatest amount of rust and which the least? Why?

Answers may vary depending on actual observations, but test tubes A, B, D, and E should show, at most, traces of rust. Test tube C should show moderate rust, and test tube F heavy rust.

Q2: What might explain some rust appearing on the nails in test tubes A or D?

Test tubes A and D both expose the nail to air, which contains both oxygen and some water vapor. That water vapor may be sufficient to cause minor rust accumulation.

Q3: What might explain some rust appearing on the nails in test tubes B or E?

No rusting can occur in the absence of oxygen, but the boiled water (tube B) and the boiled sodium chloride solution (tube E) may still contain minor amounts of dissolved air. The small amount of oxygen present may be sufficient to cause minor rusting.

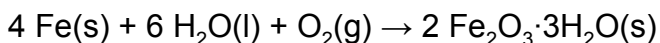
Q4: Did a chemical reaction occur between the iron and the sodium chloride in test tube F? Explain your reasoning.

No. The sodium chloride acts only as an electrolyte, which in effect catalyzes the reaction between iron and oxygen by allowing electron transfer.

The only possible chemical reaction between iron and sodium chloride would be the formation of iron chloride and metallic sodium. The activity series of metals tells us that this reaction cannot occur spontaneously.

Q4: Is the presence of sodium chloride alone sufficient to initiate or accelerate rusting? Explain your reasoning.

No. The balanced equation for the rusting reaction is:



Sodium chloride is neither a reactant nor a product in this reaction.

## Laboratory 16.3: Measure Electrode Potentials

Q1: Of the eight metals shown in Table 16-4, why did we first use copper as the reference electrode for each of the other metals?

Of those eight metals, copper is the lowest in the activity series of metals. Because we used copper as the initial reference electrode, we were able to

determine how to connect the DMM once, and use the same connection for the electrodes of other metals. If we'd used one of the other metals as the initial reference electrode, we'd have to determine how to connect the DMM each time.

Q1: Using copper as the reference electrode, rank the cell voltage for each of the other anodes you tested.

Answers may vary depending on actual observations, but from highest to lowest the cell voltages should be in the following rank order: Mg, Al, Zn, Fe, Ni, Sn, Pb. The final two metals produce voltages so close to each other that the final two positions may be equal or reversed based on experimental results.

Q3: Using the standard reduction potentials listed in Table 16-3, calculate the theoretical voltage for each of the cells you tested and recorded in Table 16-4. How do the actual voltages you measured compare to the theoretical voltages you calculated? Propose an explanation for any differences.

The theoretical values are as follows:

Mg: 2.71 V

Al: 2.00 V

Zn: 1.10 V

Fe: 0.78 V

Ni: 0.59 V

Sn: 0.48 V

Pb: 0.47 V

Observed values will be lower, primarily because resistance in the electrodes, alligator clips, and wires causes a voltage drop.

## **Laboratory 16.4: Observe Energy Transformation**

Q1: Why did the LED remain unlit with the copper/iron cell?

The copper/iron cell has a theoretical voltage of 0.78 V (and a lower actual voltage), which is insufficient voltage to illuminate the LED.

Q2: What relationship exists between the surface area of the electrodes and the voltage produced by the cell?

None. The cell produces the same voltage regardless of the size of the electrodes.

Q2: What relationship exists between the surface area of the electrodes and the current produced by the cell?

The current produced by the cell is proportionate to the surface area of the electrodes. Doubling the surface area of the electrodes doubles the current, and halving the surface area of the electrodes halves the current.

Q4: Commercial alkaline cells ("batteries") use electrodes made from zinc powder and

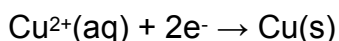
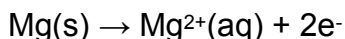
manganese dioxide powder. Why do these cells use powder rather than solid chemicals?

Using powders increases the surface area of the zinc and manganese dioxide, which also increases the current available from the cell.

### Laboratory 16.5: Build a Voltaic Cell

Q1: Which of the electrodes is the anode and which the cathode?

The two half-reactions for this cell are:



In the combined reaction, magnesium atoms lose electrons (are oxidized) to form magnesium ions and copper ions gain electrons (are reduced) to form metallic copper. In a voltaic cell, the anode is the negative electrode. Current flows into the anode (through the wire connected to the anode), and electrons flow outward, into the electrolyte.

To determine which metal forms the anode and which the cathode in this cell, we need only determine which metal is being oxidized (the anode), and which is being reduced. Because magnesium is being oxidized, it forms the anode.

Q2: At which electrode does oxidation occur?

Oxidation occurs at the magnesium electrode (the anode).

Q3: What is the purpose of the tubing filled with sodium chloride solution?

This tubing, called the salt bridge, provides an electrical path to link the two half cells, while preventing physical migration of ions between the two half cells.

Q4: If you immerse a magnesium electrode in a solution of copper sulfate, metallic copper spontaneously plates out on the electrode. If you place a copper electrode in a solution of magnesium sulfate, no such spontaneous reaction occurs. Why?

On the activity series of metals, magnesium lies far above (is much more active and more easily oxidized than) copper. If you place an active metal, such as magnesium, in a solution of a salt of a less active metal, such as copper sulfate, the easily oxidized magnesium spontaneously loses electrons to form magnesium ions. Those electrons are captured by copper ions, reducing them to metallic copper.

If you place a relatively inactive metal, such as copper, in a solution of a salt of an inactive metal, such as magnesium sulfate, no spontaneous reaction occurs because the more easily oxidized metal (magnesium) is already in the form of (oxidized) ions and the more easily reduced metal (copper) is already in the form of metallic (reduced) copper.

Q5: If you substituted an aluminum electrode for the magnesium electrode, and a silver electrode for the copper electrode, what voltage would you expect the cell to produce?

Why?

The standard reduction potential of aluminum is  $-1.66\text{ V}$  and that of silver is  $+0.80\text{ V}$ , so the theoretical voltage of this cell is  $2.46\text{ V}$ . (The actual voltage will be lower because of internal resistance.)

Q6: Did the voltage and/or current change when you altered the concentration of the electrolytes? Why or why not?

Answers will vary with experimental observations. However, within a wide range of electrolyte concentrations, the voltage of the cell should remain about the same because voltage is determined by the standard reduction potentials of the metals used as electrodes. The current of the cell may increase at higher electrolyte concentration, because the current capacity of the cell is determined both by the surface area of the electrodes and by the number of electrolyte ions available to carry the current through the cell.

### Laboratory 16.6: Build a Battery

Q1: From your measurements of voltage, resistance, and current in the cell, series batteries, and parallel batteries, what general conclusions can you draw?

Answers may vary, but in general:

- Voltage increases as you increase the number of cells in series, but the increase is not linear. For example, two cells in series produce a higher voltage than one cell, but not twice as high, and adding a third cell in series increases the voltage, but not by 50%. This reduction in voltage is due to resistance in the cell itself, as well as the wires and connectors used to join the cells.
- Resistance increases slightly more than linearly as you increase the number of cells. That is, a two-cell battery has slightly more than twice the resistance of a single cell, and a three-cell battery has more than 50% more resistance than a two-cell battery.
- Although the voltage increases in a series battery, the current actually decreases slightly. We'd expect the current to be constant in a series battery, but that disregards the effect of the increased resistance.
- A series battery increases voltage at the same current (actually, the current is slightly lower than the theoretical value due to increased resistance), while a parallel battery increases current at the same voltage (actually, the voltage is also slightly lower than the theoretical value, again due to increased resistance).

Q2: Which metal is the anode and which the cathode in these batteries? In which direction do electrons flow?

Magnesium is the anode and copper the cathode. Electrons flow through the wire into the magnesium anode and outward from the magnesium anode into the electrolyte.

Q3: A standard 12V lead-acid automobile battery when fully charged has a terminal voltage of 12.6V to 12.8V. How many magnesium/copper cells would be required to

reach at least this voltage?

Answers will vary depending on the actual voltage and current produced by the lemon cells, but the answer should take into account the reduction in voltage increase as each cell is added to the battery, caused by internal resistance.

Q4: If starting a particular automobile requires 600 amps (600,000 mA), how many of your magnesium/copper/lemon cells would be needed to construct a battery capable of starting that automobile? Would the internal resistance of the lemon battery be an issue?

Even a very large number of lemon cells would not be sufficient to produce 600 amps because of losses due to internal resistance.



## Chapter 17 – Photochemistry

### Laboratory 17.1: Photochemical Reaction of Iodine and Oxalate

Q1: Which of the light sources caused the largest and smallest visible change in the iodine/oxalate solutions? Propose an explanation.

Exact answers will vary, but in general the following should be true:

Test tube B (exposed to direct sunlight) should show the greatest and fastest change, with test tube C (open shade) showing a much smaller and much slower change.

Test tube E (fluorescent light) should show some change, but that change will be less than the change in open shade and much less than the change in the tube exposed to direct sunlight.

Test tube F (incandescent light) may show a slight change after extended exposure.

Test tube D (ambient light) should show little or no discernible change, even after extended exposure.

The amount and rate of change are determined by the intensity and wavelength of the light. Short wavelengths (ultraviolet through blue) are present in direct sunlight, open shade, and (to a smaller extent) fluorescent light, and are most effective at initiating and sustaining the iodine/oxalate reaction. Light at long wavelengths (yellow, orange, and red) has insufficient energy to initiate or sustain the reaction, regardless of intensity. Any change that occurs in the tube exposed to intense incandescent light results from the small amount of short wavelength light emitted by incandescent bulbs.

Q2: Examine the example data given in Table 17-1. What type of light source do you think was used? Do the data given for the 30 minutes and 1 hour times match what you would expect from the datum for the 15 minute exposure time? Why or why not?

This tube was exposed to what amounts to open shade (actually, it was exposed outdoors on a very cloudy day).

Test tube #1 contains the concentration of iodine that we arbitrarily labeled 100%, #2 is 50%, #3 is 25%, and so on through tube #6.

The initial 15 minute exposure reduced the iodine concentration to a value about halfway between #1 (100%) and #2 (50%), or roughly 75%, which means about 25% of the iodine reacted in 15 minutes. (Because it's difficult to estimate the density of these darker solutions with any real accuracy, at this point we'll say only that the actual concentration in that tube was probably somewhere between 65% and 85%, which means that somewhere between 15% and 35% of the iodine actually reacted.)

After a total of 30 minutes, the sample matched tube #2 (50%) closely, so we'll

revise our estimate to say that each of the first two 15-minute exposures reduced the concentration by about 30%. (From 100% to 70% after the first 15-minute exposure, and from 70% to about 49% after the second exposure.) If that's true, the concentration should be  $(0.49 \times 0.70)$  or about 34% after the third 15-minute exposure (45 minutes total), and  $(0.34 \times 0.70)$ , or about 24% after the fourth 15-minute exposure. In fact, after one hour, the concentration was slightly lower than tube #6 (3.125%), rather than the expected 24%.

What happened? Between the time we did the 30-minute check and the 1-hour check, we were working in our lab, which has no windows. When we returned to do the 1-hour check, we found that the clouds had disappeared and the sample was sitting in direct sunlight.

Q3: If you performed this experiment under a type and intensity of light that caused a very rapid reaction, would you expect to see bubbles of carbon dioxide produced in the solution? If not, why not? (Hint: do the stoichiometry to determine the limiting reagent. How might the excess reagent react?)

No bubbles will form. We neutralized the oxalic acid with excess aqueous ammonia. Carbon dioxide evolved by the iodine/oxalate reaction will immediately react with the excess aqueous ammonia to form aqueous ammonium carbonate.

Q4: If you adjusted the amounts of reactants to near stoichiometric equivalence, would your answer to Q3 change? If not, why not? (Hint: look up the solubility of carbon dioxide and run the numbers.)

Again, no bubbles will form, which we can predict as follows:

- Each test tube contains about 4.5 mL of solution (4 mL of oxalate solution plus ten drops of tincture of iodine).
- Tincture of iodine typically contains 2% iodine m/v. That means that 100 mL of tincture contains 2 g of iodine, and 10 drops (0.5 mL) contains about 0.01 g of iodine.
- The atomic mass of iodine is 126.9 g/mol, so 0.01 g of iodine is  $(0.01 \text{ g} / 126.9 \text{ g/mol}) = 7.9 \cdot 10^{-5} \text{ mol}$ .
- The balanced reaction for the equation tells us that one atom of iodine reacts to form one molecule of carbon dioxide, so  $7.9 \cdot 10^{-5} \text{ mol}$  of iodine can produce at most  $7.9 \cdot 10^{-5} \text{ mol}$  of carbon dioxide.
- The gram molecular mass of carbon dioxide is 44.0 g/mol, so  $7.9 \cdot 10^{-5} \text{ mol}$  of carbon dioxide is  $3.5 \cdot 10^{-3} \text{ g}$  (0.0035 g) of carbon dioxide.
- The solubility of carbon dioxide at room temperature and pressure is about 1.5 g/L, or about 0.0015 g/mL.
- About  $(4.5 \text{ mL} \times 0.0015 \text{ g/mL}) = 0.0068 \text{ g}$  of carbon dioxide will dissolve in 4.5 mL of solution, or roughly twice as much as is produced by the reaction.

## Chapter 18 – Colloids and Suspensions

### Laboratory 18.1: Observe Some Properties of Colloids and Suspensions

Q1: What observable physical characteristic allows you to discriminate a colloid from a suspension?

Colloidal particles do not settle under the force of gravity, but suspended particles do. Colloidal particles are passed by even the most retentive filter paper, which captures most suspended particles.

Q2: What observable physical characteristic allows you to discriminate a solution from a colloid?

Solutions do not exhibit the Tyndall Effect; colloids do.

Q3: Lunar gravity is about one sixth Earth's gravity. Might a sample that exhibits the characteristics of a suspension on the moon exhibit the characteristics of a colloid on Earth? Why?

No, although the converse is true. Suspended particles that settle under weak Lunar gravity will also settle under the much stronger gravity of earth, but some mixtures that behave as suspensions by settling under earth's gravity would behave as colloids under weaker Lunar gravity.

Q4: Some samples are difficult to classify because their physical properties are intermediate or mixed between the characteristics of solutions, colloids, and suspensions listed in Table 18-2 (for example, they may separate under the force of gravity, but very, very slowly). Why do some samples display such intermediate/mixed properties?

Because those samples are made up of particles of varying sizes and masses.

Q5: Consider a mixture of a solid material in water which clearly exhibits the properties of a suspension. If you created a similar mixture, but using a different continuous medium (such as vegetable oil), might that mixture behave as a colloid? Why?

Yes. Whether particles behave as a colloid or a suspension is determined by the size and mass of the particles, the viscosity of the continuous phase, and the molecular attractions between the particles and the continuous phase. It's quite possible that the solid material would behave as a colloidal dispersed phase in a liquid such as vegetable oil that is more viscous than water or to which the solid particles were more attracted.

### Laboratory 18.2: Produce Firefighting Foam

Q1: Why are foams like this particularly effective at putting out fires?

Such foams physically isolate the burning fuel from atmospheric oxygen, smother the fire by surrounding it with carbon dioxide gas, and cool the

combustible material below its ignition temperature.

Q2: Would a foam of carbon dioxide dispersed in water be a good choice for putting out burning sodium metal? Why or why not?

No. Sodium metal reacts with carbon dioxide gas and reacts fiercely with water.

Q3: Old-style soda-acid fire extinguishers produce not a stream of foam, but a stream of liquid. Propose an explanation.

No stabilizing agent is present in soda-acid fire extinguishers, so no foam forms. The reaction between the sodium bicarbonate and the acid produces carbon dioxide gas, which pressurizes the container, ejecting a stream of liquid from the nozzle.

### Laboratory 18.3: Prepare a Gelled Sol

Q1: What physical characteristic does a gelled sol possess that differentiates it from ordinary liquids?

Unlike a liquid, which assumes the shape of the container that holds it, a gelled sol maintains its shape even when it is not in a container.

Q2: What differences did you observe between burning napalm and burning gasoline?

Answers will vary, but should include some or all of the following:

- Napalm is considerably harder to ignite than gasoline.
- Burning napalm burns much more slowly than gasoline.
- Burning napalm does not spread as it burns.
- Burning napalm sticks to whatever it contacts.
- Burning napalm produces much more smoke than gasoline.
- Burning napalm produces a strong odor of burning plastic.
- Burning napalm leaves a shiny solid black residue.

Q3: Napalm was originally developed during WWII as an improved substitute for liquid gasoline for use in flame throwers, fire bombs, and other weapons. Based on your own observations, what advantages does napalm have as a weapon relative to liquid gasoline?

The first four or five bullet points in the preceding question are all advantages of napalm for military use. Because it's harder to ignite than gasoline, napalm is much safer to handle. Its slower burn rate means that energy is not wasted in producing fireballs, which are visually impressive but do little damage to the target. Because napalm does not spread, damage is concentrated on the actual target rather than being dissipated. Its stickiness means that it is very difficult to remove burning napalm from materials it contacts. Finally, the dense black smoke produced by napalm may be useful in obscuring the vision of enemy soldiers.

## Chapter 19 – Qualitative Analysis

### Laboratory 19.1: Using Flame Tests to Discriminate Metal Ions

Q1: Road safety flares produce a brilliant red light. Which element do you think is used to produce that coloration?

Calcium, lithium, and strontium all impart a reddish coloration to a flame, but strontium is usually used because it produces the most intense red.

Q2: A pyrotechnic produces brilliant green stars. Salts of what element or elements might be included in the pyrotechnic mixture to produce this effect?

Barium, boron, and copper(II) salts all impart a greenish coloration to a flame. All are used, alone or in combination, to produce green pyrotechnic flames.

Q3: During the Christmas season, some retailers stock fireplace logs that produce colorful flames. How might you produce such logs yourself from ordinary firewood?

You can soak firewood in concentrated solutions of various metal salts. (For Christmas greens and reds, boric acid or borax is often used to produce the greens and strontium salts from a road flare to produce the reds.) After thorough drying, these logs when burned produce long-lasting colors. Alternatively, you can simply sprinkle small amounts of the dry salts on logs before you burn them.

### Laboratory 19.2: Using Borax Bead Tests to Discriminate Metal Ions

Q1: How closely did the bead colors you observed for various metal samples correspond to the colors listed in Table 19-3? Propose an explanation for any significant differences.

Answers will vary, but should be reasonably close to the colors described in Table 19-3. Here are some possible reasons for variations:

- Contamination of the sample or inoculating loop. To eliminate contamination of the loop, dip the loop in concentrated hydrochloric acid and heat it in the hottest part of the flame until no color is present.
- Using too much or too little of the sample. If you use too much of the sample, the bead will turn cloudy or opaque instead of remaining transparent. If you use too little, the colors may be pale or absent.
- Improper heating may yield beads that have unexpected colors. Make sure to know which is the oxidizing part of the flame and which the reducing. Allow the beads to cool thoroughly before attempting to judge their cold color.

Q2: Copper chromate is used as wood preservative for “pressure-treated” wood. What bead colors would you expect if you applied the borax bead test to a sample of copper chromate?

When we did this trial, we observed the following colors:

- Reducing flame; hot bead – green
- Reducing flame; cold bead – brown
- Oxidizing flame; hot bead – yellow-green
- Oxidizing flame; cold bead – blue-green

Q3: Copper ferrocyanide is used in water analysis and treatment. What bead colors would you expect if you applied the borax bead test to a sample of copper ferrocyanide?

When we did this trial, we observed the following colors:

- Reducing flame; hot bead – very pale green
- Reducing flame; cold bead – brown
- Oxidizing flame; hot bead – yellow-green
- Oxidizing flame; cold bead – blue-green

### **Laboratory 19.3: Qualitative Analysis of Inorganic Anions**

Q1: The precipitates produced by the anion tests take some time to settle. What alternative procedures might you use to minimize the time necessary?

If you have access to a centrifuge, that is by far the best solution. If you're working with relatively large samples, you can use filtration to separate the solid precipitate from the supernatant liquid.

Q2: Why did we wash the precipitate in step 10?

The precipitate contains silver halide salts, which we'll analyze further in later steps. The supernatant fluid contains other anions which might interfere with those later tests. By washing the precipitate, we remove those other anions.

Q3: If silver nitrate were unavailable to you, what alternative reagent or reagents might you use to detect and discriminate among the halide anions? (Hint: look up the solubility of the various halide salts to find other insoluble halides.)

Halide salts are readily soluble, with the exceptions of silver, lead(II), and mercury(I) halides. Lead(II) halides are thousands of times more soluble than the corresponding silver halides, so lead(II) is poor choice for the precipitating reagent. Mercury(I) halides are even less soluble than silver halides, so mercury(I) nitrate would be a good choice for the precipitating reagent. Of course, mercury salts are expensive, difficult to obtain, and extremely toxic, which is why silver nitrate is generally used for this purpose.

### **Laboratory 19.4: Qualitative Analysis of Inorganic Cations**

Q1: Examine the matrix you filled in for Table 19-5. Which, if any, of the cations cannot be unambiguously identified using only the five primary reagents?

Consider first the reaction of each anion with sulfuric acid, hydrochloric acid, sodium hydroxide, and aqueous ammonia:

	<b>H<sub>2</sub>SO<sub>4</sub></b>	<b>HCl</b>	<b>NaOH</b>	<b>NH<sub>3</sub></b>
Al <sup>3+</sup>	no reaction	no reaction	white gelatinous ppt; soluble in excess NaOH or acids	white gelatinous ppt; soluble in excess NH <sub>3</sub> or acids
Ag <sup>+</sup>	no reaction in dilute Ag <sup>+</sup> sltn; otherwise, white ppt	white ppt; soluble in NH <sub>3</sub> ; insoluble in nitric acid	brown ppt; insoluble in excess NaOH	brown ppt; soluble in excess NH <sub>3</sub> to yield colorless sltn
Ba <sup>2+</sup>	white ppt	no reaction	no reaction if Ba <sup>2+</sup> < 0.2M; otherwise fine white ppt	no reaction if Ba <sup>2+</sup> < 0.2M; otherwise fine white ppt
Ca <sup>2+</sup>	no reaction unless Ca <sup>2+</sup> concentration is high; otherwise, white ppt	no reaction	no reaction if Ca <sup>2+</sup> < 0.02M; otherwise fine white ppt	no reaction
Co <sup>2+</sup>	no reaction	no reaction	blue or red ppt; insoluble in excess NaOH, but soluble in acids	blue or red ppt; soluble in excess NH <sub>3</sub> to yield brown sltn
Cr <sup>3+</sup>	no reaction	no reaction	gray-green ppt; soluble in excess NaOH	gray-green ppt; insoluble in excess NH <sub>3</sub>
Cu <sup>2+</sup>	no reaction	no reaction	light blue ppt; insoluble in moderate excess of NaOH	light blue ppt; soluble in excess NH <sub>3</sub> to yield blue sltn
Fe <sup>2+</sup>	no reaction	no reaction	white gelatinous ppt; insoluble in excess NaOH	white gelatinous ppt; insoluble in excess NH <sub>3</sub>
Fe <sup>3+</sup>	no reaction	no reaction	red-brown ppt; insoluble in excess NaOH	red-brown ppt; insoluble in excess NH <sub>3</sub>
Mn <sup>2+</sup>	no reaction	no reaction	light pink ppt; insoluble in excess NaOH	light pink ppt; insoluble in excess NH <sub>3</sub>
Ni <sup>3+</sup>	no reaction	no reaction	green gelatinous ppt; soluble in	green gelatinous ppt; soluble in

			excess NaOH	excess $\text{NH}_3$ to yield a blue sltn
$\text{Pb}^{2+}$	white ppt	initially, no reaction; after several minutes, a fine white ppt	white ppt; soluble in excess NaOH	white ppt; insoluble in excess $\text{NH}_3$
$\text{Sr}^{2+}$	white ppt	no reaction	no reaction	no reaction
$\text{Zn}^{2+}$	no reaction	no reaction	white gelatinous ppt; soluble in excess NaOH	white gelatinous ppt; soluble in excess $\text{NH}_3$

From these observations, we can draw the following conclusions about each of the listed cations. (Note that the presence of other cations may interfere with identifying those on this list.)

- $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  can be unambiguously discriminated from the other ions but not from each other using only the primary reagents.
- $\text{Ag}^+$  can be unambiguously discriminated by its characteristic reactions with the primary reagents.
- $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$  can be unambiguously discriminated from the other ions but not from each other using only the primary reagents.
- $\text{Co}^{2+}$  can be unambiguously discriminated by its characteristic reactions with the primary reagents. Depending on the anions present,  $\text{Co}^{2+}$  may with hydroxides form either a blue precipitate, which may be confused with  $\text{Cu}^{2+}$ , or a red precipitate, which may be confused with  $\text{Fe}^{3+}$  or  $\text{Mn}^{2+}$ . If the precipitate is blue,  $\text{Co}^{2+}$  can be discriminated from  $\text{Cu}^{2+}$  by observing the behavior of the precipitate in excess aqueous ammonia. The blue  $\text{Cu}^{2+}$  precipitate dissolves in excess ammonia to form a bright blue solution, whereas the blue  $\text{Co}^{2+}$  precipitate dissolves to form a brown solution. The reddish precipitates of  $\text{Fe}^{3+}$  or  $\text{Mn}^{2+}$  are insoluble in excess ammonia, while the reddish  $\text{Co}^{2+}$  precipitate dissolves to form a brown solution.
- $\text{Cr}^{3+}$  can be unambiguously discriminated by the characteristic gray-green precipitate it forms with sodium hydroxide and aqueous ammonia.
- $\text{Cu}^{2+}$  can be unambiguously discriminated by the characteristic blue precipitate it forms with sodium hydroxide and aqueous ammonia, and because that precipitate dissolves in excess aqueous ammonia to produce an intensely blue solution.
- $\text{Fe}^{2+}$  can be unambiguously discriminated by the fact that the gelatinous white precipitates it forms with sodium hydroxide and aqueous ammonia are insoluble in an excess of either reagent.
- $\text{Fe}^{3+}$  can be unambiguously discriminated by the reddish-brown precipitates it forms with sodium hydroxide and aqueous ammonia.



- $\text{Mn}^{2+}$  can be unambiguously discriminated by the very pale pink precipitates it forms with sodium hydroxide and aqueous ammonia.
- $\text{Ni}^{3+}$  can be unambiguously discriminated by the gelatinous green precipitates it forms with sodium hydroxide and aqueous ammonia.
- $\text{Pb}^{2+}$  can be unambiguously discriminated using all four of the primary reagents. Although several other cations produce white precipitates with sulfuric and/or hydrochloric acids, the reactions of  $\text{Pb}^{2+}$  with sodium hydroxide and aqueous ammonia serve to discriminate it from those other ions.

Q2: If any of the cations cannot be unambiguously identified using only the five primary reagents, can they be identified using one or more of the secondary reagents? If so, which secondary reagents are useful for identifying which cations?

- $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  can be discriminated by using potassium ferrocyanide, with which  $\text{Al}^{3+}$  gives no reaction and  $\text{Zn}^{2+}$  forms a fine gray or blue gray precipitate.
- $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$  cannot be discriminated from each other using the secondary reagents available.

Q3: If you have a sample that is known to contain only iron(II) and/or iron(III) and/or copper(II) cations, what is the minimum number and identity of the reagents needed to identify unambiguously the cations present in the unknown? What characteristic reactions would serve to discriminate these three cations?

Aqueous ammonia precipitates all three of these ions, producing with iron(II) ions a white, gelatinous precipitate, iron(III) ions a red-brown precipitate, and copper(II) ions a blue precipitate, but if two or all three ions are present it may be difficult to identify the mix of ions from the appearance of the precipitate.

To identify the specific mix present, take the following steps:

- when you have added sufficient aqueous ammonia to precipitate all of the ions present, continue adding aqueous ammonia until you added a total of twice the amount required to precipitate all of the ions. If some or all of the precipitate dissolves and the solution assumes a blue color, copper(II) ions are present in the sample.
- to another portion of the sample, add a few drops of potassium ferricyanide. A deep blue precipitate confirms the presence of iron(II) ions.
- to another portion of the sample, add a few drops of potassium thiocyanate. If the solution turns a deep red color, that confirms the presence of iron(III) ions.

## Laboratory 19.5: Qualitative Analysis of Bone

Q1: Considering the results of your tests, name and give formulae for the compounds you believe may be present in the bone sample.

Answers will vary depending on the type of sample used, but bone is primarily made up of complex calcium phosphates in the form of hydroxylapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ). The sodium and chloride ions are present as sodium

chloride ( $\text{NaCl}$ ) in solution in cells, and tests for both of those ions should be positive. (In fact, the flame test for sodium is so sensitive, that it will be positive on most samples of nearly anything.) The calcium and sulfate ions are present as calcium sulfate ( $\text{CaSO}_4$ ), and tests for both of these ions should be positive.

Iron(III) ions are present in the hemoglobin in bone marrow, and the sample should test positive for these ions. Tests for ammonium and potassium ions may or may not be positive, depending on the sample.

Q2: If a sample produces a precipitate when treated with silver nitrate, how would you proceed to establish unambiguously that the precipitate is silver chloride rather than silver bromide or silver iodide?

Silver chloride is soluble in 6 M aqueous ammonia; silver bromide and silver iodide are not.

Q3: Is it possible to test the dissolved bone sample to determine if carbonate ion was present in the original solid sample? If not, explain why and devise a test procedure to determine if a solid bone sample contains carbonate ions.

No, it is not possible to test the dissolved bone sample for carbonate ions. When the sample dissolves in nitric acid, any carbonates present react with the nitric acid to form carbon dioxide gas, which is lost.

You can test the original sample for carbonate ions by dissolving it in nitric acid in a gas generating bottle (or a similar apparatus made with a test tube, one-hole stopper, and glass tube) with tubing leading any gas that is evolved into a saturated solution of barium hydroxide. If any gas is evolved, it is likely to be carbon dioxide. If the gas reacts with the saturated barium hydroxide solution to form a white precipitate (or even if the solution just turns cloudy), the presence of carbon dioxide (and, therefore, carbonates in the original sample) is confirmed.

## Chapter 20 – Quantitative Analysis

### Laboratory 20.1: Quantitative Analysis of Vitamin C by Acid-Base Titration

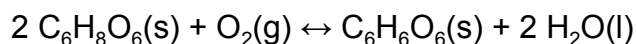
Q1: How closely did the mass of vitamin C you determined experimentally correspond to the nominal mass of vitamin C listed by the manufacturer?

Answers will vary, but FDA regulations mean that the actual vitamin C content of a tablet should be very close to the nominal content. Experimental results should be within a few percent of nominal.

Q2: What percentage of the tablet's mass is vitamin C and what percentage of its mass is binder and other inert ingredients?

Answers will vary, depending on the specific sample tested.

Q3: Ascorbic acid and atmospheric oxygen can react spontaneously by the following redox reaction



If this reaction occurred before you completed the titration, how might it affect your results?

Oxidation of the vitamin C reduces the amount of vitamin C and should result in an experimental value lower than the nominal value stated for the sample.

Q4: When chemists use titration for quantitative analysis, they ordinarily repeat the titration several times. Why?

Experimental errors tend to be small and random, so experimentally-determined values are equally likely to be higher or lower than the actual value. Doing repeated titrations and averaging the values tends to eliminate these random errors, giving an experimental value closer to the actual value.

Also, if a gross experimental error produces a result far from the actual value, doing a second titration makes it immediately obvious that one or both of those values is erroneous. A third titration should closely match one of the first two, making it obvious which of the first two results should be discarded.

### Laboratory 20.2: Quantitative Analysis of Chlorine Bleach by Redox Titration

Q1: How closely does your experimental value for the mass percentage of sodium hypochlorite in the chlorine bleach sample correspond to the mass percentage on the label? Give at least three possible sources of error that might explain any discrepancy.

Answers will vary depending on the sample used, but the experimental value should correspond quite closely with the nominal value. We titrated three samples of chlorine bleach from newly-opened bottles, including a name-brand

5.25% bleach, a store-brand 5.25% bleach, and a name-brand “ultra” 6.0% bleach. We determined the hypochlorite content of the the name-brand 5.25% bleach to be 5.31%, the store-brand 5.25% bleach to be 5.39%, and the name-brand 6.0% bleach to be 6.08%.

Here are some possible errors:

- Using a sample from a container that has been opened and used for some time may give experimental values noticeably different from nominal values.
- Volumetric or gravimetric errors in determining the density of the bleach sample may give experimental values that are higher or lower than the actual and/or nominal values.
- Using sodium thiosulfate titrant that has not been standardized may give values different from the actual and/or nominal values.
- Sodium thiosulfate is not stable in solution, so using anything other than a freshly made up solution may give erroneous experimental values.
- Titration errors caused by poor working procedures or an uncalibrated burette yield experimental values that are higher or lower than the actual and/or nominal values.

Q2: How would you modify the procedure in Part II to determine the sample size gravimetrically rather than volumetrically? What advantage or advantages would substituting a gravimetric procedure confer?

Rather than using a pipette to measure and transfer the bleach sample to the reaction flask, place the reaction flask on your balance, tare the balance, and use a dropper to transfer a measured mass of bleach (~ 2 to 2.5 g) to the reaction flask.

Using a high-resolution balance to measure reactants gravimetrically rather than volumetrically provides higher accuracy.

Q3: Why did we use back titration rather than forward titration for this quantitative analysis?

Using forward titration is impossible. We would have to judge the end point by determining when a very dark brown solution stopped getting darker brown. Using back titration allows us to determine the end point by judging when the intense blue color of the starch-iodine indicator disappears, which is much easier to judge.

### **Laboratory 20.3: Quantitative Analysis of Seawater**

Q1: How do the values for chloride and sulfate ion concentrations you determined experimentally compare with the standard values given in the introduction? If the values differ significantly, propose at least one explanation. (Reasonable explanations may differ depending on whether you're using natural or synthetic seawater.)

Answers will vary, depending on the sample used. We ran the analyses on two

samples, one of actual sea water from near Myrtle Beach, South Carolina and the other made up from a bottle of sea salt we found in the kitchen condiments aisle at Costco, with which we made up artificial seawater by dissolving sufficient sea salt to reach the nominal concentration of seawater. Both samples tested as having chloride and sulfate concentrations within a few percent of nominal.

Other than experimental error (see the next question), there are numerous reasons why experimental values may differ from nominal. Natural seawater varies significantly in concentration, depending on location, time of year, and many other factors. For example, natural seawater has lower salt concentration near the mouths of rivers. Conversely, seawater gathered from a tidal pool may be significantly more concentrated than nominal, as may seawater gathered at the surface on a hot day. Artificial seawater may vary dramatically depending on the sample. Our Costco sea salt was labeled as natural sea salt from the Mediterranean Sea, but some “sea salt” products (including “instant ocean” type products sold in aquarium stores) may actually be entirely artificial.

Q2: List at least five possible sources of experimental error.

Here are several possible sources of experimental error:

In Part I:

- Failure to filter the natural seawater sample to remove algae and other suspended solid matter, leading to an erroneously high value for total dissolved solids.
- Volumetric error in measuring the seawater sample, leading to an erroneous value for density and total dissolved solids.
- Failure to do a quantitative transfer, leading to an erroneously low value for total dissolved solids.
- Failure to evaporate the sample to dryness, leading to an erroneously high value for total dissolved solids.
- Gravimetric error in determining the mass of the total dissolved solids.

In Part II:

- Volumetric error in measuring the sample aliquot.
- Volumetric or gravimetric error in making up the silver nitrate titrant.
- Titration errors caused by improper procedure or an inaccurate or uncalibrated burette.

In Part III:

- Volumetric error in measuring the sample aliquot.
- Adding insufficient barium nitrate solution to fully precipitate the sulfate ions present in the sample.
- Gravimetric error in determining the initial mass of the filter paper.

- Failure to dry the filter paper and barium sulfate thoroughly.
- Gravimetric error in determining the mass of the filter paper and barium sulfate.

Q3: Other than sodium, the two cations that are present in the highest concentrations in seawater are magnesium (1.17%) and calcium (1.13%). Look up the solubility product constants for magnesium and calcium in combination with various anions and use that information to choose a common reagent anion that could be used to selectively precipitate magnesium while leaving calcium in solution. Choose another common reagent anion that could be used to selectively precipitate calcium ions while leaving magnesium ions in solution.

Hydroxide is one common reagent anion that can be used to selectively precipitate magnesium while leaving calcium in solution. Carbonate is one common anion that can be used to selectively precipitate calcium while leaving magnesium in solution.

## Chapter 21 – Synthesis of Useful Compounds

### Laboratory 21.1: Synthesize Methyl Salicylate from Aspirin

Q1: How did your actual yield compare to the theoretical yield? Propose at least five possible explanations for the actual yield being smaller than theoretical.

Results will vary, but the actual yield should be >70% of theoretical. Among the most common reasons for lower than expected yields are:

- measurement errors
- the presence of water, which inhibits the reaction
- impure reactants
- not having methanol in sufficient excess
- not allowing sufficient time for the reaction to run to completion
- running the reaction at too low a temperature
- evaporation losses
- losses during washing (methyl salicylate is slightly soluble in water)

Q2: Why did we use ice-cold water to extract impurities from the product?

Methyl salicylate is slightly soluble in water, and more soluble in hot water than cold. Using ice-cold water minimizes the amount of methyl salicylate that dissolves in the wash water.

Q3: If we had used salicylic acid, would you expect the percent yield to be higher, lower, or the same as the percent yield using aspirin? Why?

On a mole basis, the theoretical yield is the same whether you use aspirin or salicylic acid as the reactant, because each mole of aspirin reacts to form one mole of salicylic acid, which subsequently reacts with methanol to form one mole of methyl salicylate. In practice, the actual yield will be lower using aspirin than it would have been using salicylic acid. The raw product will also be less pure using aspirin, because it will contain a mix of methyl salicylate and methyl acetate, formed by the acetyl group released when the aspirin reacts initially to form salicylic acid.

Q4: Aspirin that is very old or has been stored improperly often has a strong odor of vinegar. On that basis, what ester other than methyl salicylate would you expect to be present in your crude product?

Vinegar is simply dilute acetic acid, and acetic acid is one of the decomposition products of aspirin. If acetic acid is present in the reaction mixture, you would expect that one of the minor products would be the ester methyl acetate.

Q5: Did your tests show a sharp freezing/melting point? If not, what does this suggest about the purity of your product?

Results will vary, although reasonably pure methyl salicylate should have a relatively narrow freezing/melting range, at most a few degrees. A broad freezing/melting range indicates that the product is very impure.

## **Laboratory 21.2: Synthesize Rayon Fiber**

Q1: What compound forms the powder-blue precipitate when you add sodium hydroxide solution to the copper sulfate solution?

Copper(II) hydroxide.

Q2: What compound produces the intense blue color when the powder-blue precipitate is dissolved in excess aqueous ammonia?

Tetraaminocopper(II) hydroxide.

Q3: Would you expect the solid rayon you produced to be soluble or insoluble in a solution of tetraaminocopper(II) hydroxide? Why?

Soluble. Rayon is simply reconstituted cellulose, and so is as soluble in tetraaminocopper(II) hydroxide solution as the paper used as the original source of the cellulose.

Q4: Is copper sulfate consumed in this reaction, or could it be recycled from the spent cellulose solution? If the latter, propose a general method for reclaiming and reusing the copper.

Copper sulfate is not consumed, and could be reclaimed/recycled from the spent solution. In practice, the spent solution is evaporated until it is saturated, and then concentrated aqueous ammonia is added as necessary to reform the tetraaminocopper(II) hydroxide.

Q5: Structurally and chemically, rayon resembles the natural fiber cotton, and in fact rayon can be dyed, Mercerized, and otherwise treated using many of the same finishing processes that are used for cotton. Based on your examination of your product, why, then, would anyone go to the trouble of producing rayon rather than just using natural cotton fiber?

As a natural product, cotton fibers are available in a very narrow range of lengths, thicknesses, and shapes, factors influenced by the type of cotton plant, the growing conditions, and, to some extent, by how the raw fiber is processed. Because Rayon is produced from a solution of cellulose, Rayon fibers can be made in any arbitrary length, thickness, or shape, which allows the manufacturer to optimize the fiber characteristics for the fabric to be made from that fiber. For example, one of the first uses of Rayon was to produce artificial silk for women's stockings, an application for which natural cotton is much too coarse.



## Chapter 22 – Forensic Chemistry

### Laboratory 22.1: Use the Sherlock Holmes Test to Detect Blood

Q1: You perform this test on a control sample that is known not to contain blood, but the test results are positive. What might the sample contain that produces the false positive results?

The Kastle-Meyer presumptive test for blood is highly selective, but there are some materials that may cause false positives. Among these are chemical oxidizers, some vegetable enzymes (particularly those present in cucumber, horseradish, potato, and tomato), some fruit extracts, some metallic substances, and any substance that contains peroxidase-like enzymes.

Q2: As a forensic specialist, you are provided with a sample and asked to use this test to determine whether or not blood is present. You know that you will have to testify in court about the results of your test. Other than testing the sample itself, what other actions might you take to ensure that your testimony is accepted as valid?

Establish and maintain a chain of custody. Document the reagents and procedures used, and the steps taken to ensure that the reagents were fresh and uncontaminated and that no contaminants that might produce false positives could have been introduced during the testing procedures. Run the tests using the same reagents and procedures against a sample known to contain blood.

### Laboratory 22.2: Perform a Presumptive Test for Illicit Drugs

Q1: You have used Marquis Reagent to test a sample that is suspected to contain codeine. The reagent yields a purple color, which apparently confirms that codeine is present, but the purple color is less intense than you expected. Using the reagents you have on hand, what might you do to verify or disprove the positive Marquis test?

Test another portion of the sample with concentrated nitric acid. If codeine is present, the nitric acid test yields a light greenish-yellow color.

Q2: You have a sample that you suspect contains morphine or opium, but not both. Which reagent would you use to discriminate between the two? If the sample tested negative for morphine, would you run additional presumptive tests? If so, why, and which test or tests would you run?

Marquis Reagent and nitric acid are both primary presumptive tests for both morphine and opium. Marquis reagent produces a “Very deep reddish purple” color with morphine, and a “Dark grayish reddish brown” color with opium. Nitric acid produces a “Brilliant orange yellow” color with morphine, and a “Dark orange yellow” color with opium.

These colors are sufficiently different that it is relatively easy to discriminate between the two compounds by comparing the test results against a standard color chart. However, the colors are sufficiently close with either reagent that if the test is positive it may be desirable to run a confirmatory test to verify that

morphine is not present. Ferric chloride reagent is a primary test for morphine, with which it produces a “Dark green” color. Because ferric chloride produces no color change with opium, it can be used to discriminate with some high level of certainty between morphine and opium.

### **Laboratory 22.3: Reveal Latent Fingerprints**

Q1: What common household substance is also used to reveal latent fingerprints? (Hint: search the Internet for cyanoacrylate.)

Superglue.

Q2: Other than primates, very few mammals have fingerprints. There is one mammal, though, that is not a primate but produces fingerprints that are almost impossible to discriminate from human fingerprints, even using current instrumental methods. What is this mammal? (Hint: search the Internet for “mammal” and “fingerprints”.)

Koalas are the only mammals other than primates that have fingerprints. Not only do koalas have fingerprints, but their fingerprints are difficult or impossible to distinguish from human fingerprints. Just as is true of human and other primate fingerprints, koala fingerprints are unique.

### **Laboratory 22.4: Use the Marsh Test to Detect Arsenic or Antimony**

Q1: The mean lethal dose of arsenic in humans is variously estimated at between 1 mg/kg (0.001 g per 1,000 g) and 3 mg/kg. You know that the Marsh Test can detect arsenic in amounts as small as 1  $\mu\text{g}$  (0.000001 g). A murder has taken place, and arsenic poisoning is suspected. You are tasked with using the Marsh Test to determine whether or not arsenic was the murder weapon. The victim weighed 100 kg, and you have only a 10 g sample of the victim's stomach contents to work with. If arsenic was used to kill this victim, is the Marsh Test sensitive enough to detect the arsenic? If so, and assuming that the victim died from a dose of only 1 mg/kg, how much smaller could your sample be and still yield usable results? If not, how much larger a sample would you require?

To answer this question, we have to make the simplifying assumption that the arsenic is evenly distributed throughout the 100 kg mass of the victim. On that basis, each 1 kg sample contains 1 mg of arsenic, and a 10 g sample contains 0.01 mg, or 10  $\mu\text{g}$ . That is ten times the threshold level for the Marsh Test, so in theory we could still detect arsenic if our sample mass was only 1 g.

Q2: Regulations restricting the use of CCA are becoming more common because of concerns that the CCA may leach out of the treated wood and into the surrounding soil. Tests have detected arsenic levels as high as 14 ppm in soil that is in contact with CCA-treated landscape timbers. If the Marsh Test can detect arsenic in amounts as small as 1  $\mu\text{g}$ , how large a soil sample would you need to use the Marsh Test successfully?

Another way to express 14 ppm is as 14  $\mu\text{g}$  per 1,000,000  $\mu\text{g}$ , or 14  $\mu\text{g}$  per g. We'd therefore need a sample mass of 1/14 g, or about 71 mg.